The development of a continuous reactor for the acid hydrolysis of cellulose and its application to refuse disposal

Thesis

THE DEVELOPMENT OF A CONTINUOUS REACTOR FOR THE ACID HYDROLYSIS OF CELLULOSE AND ITS APPLICATION TO REFUSE DISPOSAL

by

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ABSTRACT

Refuse disposal in metropolitan areas is becoming increasingly difficult and expensive as ever-greater volumes of waste need to be transported to increasingly remote landfill sites. Acid hydrolysis offers an attractive alternative means of disposal, by aiming to convert the cellulose in the waste to glucose, for fermentation to ethanol. Recent research into the hydrolysis of cellulose at elevated temperatures and short reaction times has shown that high yields of glucose may be obtained: but experimental work with refuse has been lacking.

This work describes the development of a continuous reactor for carrying out the hydrolysis of refuse under the conditions required for the determination of reaction rate data. An existing rig was modified through a series of preliminary experiments: after this, detailed testwork was carried out with filter paper, newsprint and air-classified lights of municipal refuse as cellulosic substrates, as well as pure glucose, to investigate the decomposition reaction. High yields of glucose were obtained from experiments with newsprint and refuse, and the kinetic parameters derived were compared with those of previous researchers.

The data obtained from the hydrolysis of the refuse sample was used to draw up a preliminary design of a 500 tonne/day plant to treat the air-classified light fraction of municipal refuse. The initial capital investment was estimated to be £8.1 million, and under present market conditions, it was shown to be advantageous to convert the cellulosic fraction of refuse into ethanol rather than RDF pellets. A rough estimate of a complete process to produce ethanol from untreated refuse indicated that considerable savings in overall disposal costs could be made, compared with disposing of the waste in the usual way, by landfilling after shredding or pulverisation.

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INTRODUCTION

1.1 Statement of the Problem

The satisfactory disposal of municipal solid waste or refuse in metropolitan areas of Britain has become a matter of increasing concern in recent years to local authorities and national government alike. Greatly increased volumes of waste are being produced as a result of higher living standards, and they must be disposed of safely without polluting the environment or endangering public health. Traditionally, most of Britain's refuse has been disposed of by landfilling, but as cities expand and more land is earmarked for housing development, it becomes increasingly difficult to find suitable landfill sites near centres of waste generation to replace those that are being rapidly exhausted. Transporting refuse to distant landfill sites is one option being pursued, but this adds to the complexity of the operation, and its cost. Incineration, once thought to be the cure-all of waste disposal problems in Britain, has been found to have its problems too. The need to develop alternative methods of disposal is pressing.

At the same time, and especially since the oil crisis of the early 1970s, municipal refuse has been attracting considerable attention from another quarter, for a completely different reason.The growing awareness that the earth's resources are clearly finite has led to a steadily increasing interest in the recovery of materials and energy from solid wastes - and from municipal solid waste in particular. Refuse, which is generated in large quantities and has the advantage of an established collection system, is an ideal substrate for possible resource recovery. It contains many usable commodities (such as paper, glass, metals and plastics) which may be extracted and reprocessed for the manufacture of

new products, as well as a mixture of combustible materials which may be used as fuel or converted into other useful forms of energy or raw materials for the chemical industry.

Recycling some of the materials contained in refuse, or recovering the energy of the combustible fraction, constitutes an attractive alternative means of disposal, as it would not only relieve some of the burden on landfill sites by reducing the mass and volume of waste that must ultimately be discarded, but would offer in its place a very useful resource recovery opportunity. In many countries throughout the world now, experimental programmes are under way to evaluate the various different schemes that have been put forward for resource recycling or energy recovery from refuse. To date, progress has been most rapid in the development of mechanical sorting systems for separating various materials from mixed refuse for recycling; but in recent years, with escalating oil prices as the driving force, the emphasis has been shifting more and more to the investigation of processes for recovering energy from refuse.

The present work is concerned with one such refuse-to-energy conversion process, namely, dilute acid hydrolysis. This process is aimed at converting the cellulose (found mostly in the paper and paper products which make up a significant proportion of typical municipal solid waste) in refuse to glucose, for subsequent fermentation by yeast. The final target product is ethanol, which is a clean, convenient liquid fuel as well as a potential feedstock for the production of many of the chemicals presently derived from oil. Other valuable chemicals besides could be recovered as byproducts of the hydrolysis reaction.

The hydrolysis of cellulose to fermentable sugar is not a new process, but has been used in the past, chiefly for the production of ethanol from wood residues. The traditional technology is the semi-batch percolation process, in which a stationary bed of wood chips is contacted with successive batches of hot dilute acid, at temperatures of 150° to 180°C and residence times of up to three hours. When applied to refuse treatment, however, it is envisaged that the hydrolysis be carried out in a continuous reactor operated at higher temperatures and much shorter

reaction times.

This idea stems from a consideration by Porteous (1967) of a kinetic study undertaken by Saeman (1945) into the hydrolysis of wood. Extrapolating Saeman's results to higher temperatures, Porteous predicted that yields of glucose comparable to those produced in the traditional wood hydrolysis processes could be obtained in very much shorter reaction times (of the order of a minute) if the temperature were raised from 150° to 180°C to about 240°C. This would effectively transform the slow batch hydrolysis process into a rapid continuous one, and would allow a plug flow reactor to be used in place of the traditional batch percolators, resulting in considerable savings in capital outlay. Applying the process to refuse disposal would bring the additional benefit of the savings in disposal costs that would be made. Economic evaluations of a process plant designed around this idea have repeatedly suggested that ethanol production from the wastepaper content of refuse should offer a viable means of refuse disposal (Porteous,1967,1975; Converse et al,1973; Grethlein,1978; Emery and Kent,1979; Rugg and Brenner,1980).

Since Porteous announced his new process in 1967, a number of researchers have verified his predictions that significant yields of glucose can be obtained from the hydrolysis of cellulose at high temperatures and short reaction times. But investigators have generally carried out their experiments with pure or relatively pure cellulosic substrates: and have obtained kinetic values which differ, sometimes widely, from one investigator to the next. Problems have also been encountered with the development of a continuous reactor, which mostly relate to the high temperatures and pressures required to carry out the hydrolysis swiftly, and to the fact that glucose is itself decomposed on exposure to hot mineral acids, thereby detracting from the yield of hydrolysis product. For economical operation, the decomposition must be kept at a minimum by very accurate control of the reaction parameters, a task made necessarily more difficult by virtue of the very small residence time of material in the reactor.

Only one group of researchers, Thompson and Grethlein (1979), of the Thayer School of Engineering Dartmouth College, New Hampshire have

published any kinetic results obtained from experiments with a laboratory scale plug-flow reactor at the high temperatures proposed by Porteous; these are for the hydrolysis of Solka-Floc (a purified cellulose) and newsprint. Previously at Thayer, Converse et al. (1973) had constructed and operated a continuous reactor to investigate the hydrolysis of refuse, but had been unable to maintain a constant temperature and steady flow rate during their experiments. The yields of glucose were quite low, and were not repeatable, as the reaction parameters could not be set in advance. Rugg and Brenner (1980) of New York University's Department of Applied Science have developed an extruder reactor for the hydrolysis of sawdust and paper pulp at high temperatures, but have not published any kinetic results. Other researchers have also constructed continuous reactors for cellulose hydrolysis, but at lower temperatures than those proposed by Porteous. As far as is known, outside of the present work, the kinetics of refuse hydrolysis have never been properly investigated in a continuous reactor.

The importance of obtaining kinetic data for the acid hydrolysis of cellulose in refuse and of showing that the reaction may be carried out in a continuous reactor cannot be overstated, if this process is ever to be considered seriously as a credible alternative means of municipal waste disposal. To date, engineering designs and economic appraisals of refuse hydrolysis plants have always been based on mass and energy balances obtained from the hydrolysis of pure cellulosic materials. But this is not really good enough, especially when the differences in the kinetic values to be found in the literature are known to be so considerable. In addition, refuse is an extremely unhomogeneous product, containing a great many impurities, and some of these could well influence the course of the hydrolysis reaction. It is a possibility that cannot be ruled out, and which needs to be investigated. At the same time, it would be worthwhile comparing the kinetics of refuse hydrolysis with that of purer and more easily studied cellulosic substrates, such as filter paper and newsprint, to determine whether anything at all may be inferred about the former from the latter. Only when the kinetics of the acid hydrolysis of cellulose in refuse have been properly studied and understood, will it be posible to draw up mass and energy balances upon which reliable cost estimates of a full-scale hydrolysis plant may be made.

1.2 Objectives of the Present Work

In the Engineering Mechanics Discipline of the Open University in Milton Keynes, a research programme has been under way since 1976 to develop a continuous reactor for the acid hydrolysis of cellulose in refuse. A flow reactor was designed and constructed, and operated to produce hydrolysate for fermemtation studies (Porteous and Anderson,1980;Anderson, 1981); but problems with blockages and heating, and inadequate temperature measurement and control made it impossible to obtain kinetic information about cellulose hydrolysis from this rig.

The primary aim of the present work, therefore, was to modify this equipment so as to permit the hydrolysis of cellulose to be performed under previously determined, carefully controlled conditions; and to use the modified rig to undertake a kinetic study of the hydrolysis of cellulose at elevated temperatures using dilute sulphuric acid as catalyst. The purpose of this study was to determine the optimum reaction parameters (i.e. acid concentration, temperature and reactor residence time) for maximum glucose yield, and to obtain kinetic parameters to corroborate the work of Thompson and Grethlein (1979). The feedstocks chosen for investigation were filter paper (which, being pure cellulose, could be used as a "control"), newsprint (a typical domestic waste, and one which the public is used to collecting for recycling) and refuse - this last being a sample of air-classified lights from a plant which produces refuse-derived fuel.

A second aim of this work was to use the information obtained about the hydrolysis of refuse to draw up a preliminary plant design for a refuse hydrolysis plant, and an order-of-magnitude cost estimate.

CHAPTER 2

THE DISPOSAL OF MUNICIPAL SOLID WASTE - PRESENT PRACTICE AND PROPOSED ALTERNATIVES

2.1 Introduction

Waste is a fact of life, and the problem of disposing of large quantities of waste, which is a feature of modern industrial society, is largely due to the style and standard of living that such a society enjoys. Earlier civilizations, like the ancient Greeks and Romans, were able simply to throw their waste onto the floors of their houses, and cover it with layers of earth; when too much waste and earth accumulated, they either raised the roof or moved (Alter and Dunn,1980,chap1). Such a simple solution to this perennial problem would hardly be feasible in today's highly populated and increasingly urbanised world! Especially as industrial growth and the consumer society have given rise to wastes of ever increasing complexity, which need to be disposed of safely, as well as efficiently and economically, because of the potential threat they pose to the environment and to health.

This chapter examines the problem of municipal solid waste disposal in Britain - the quantities of waste arising, its composition, and the methods presently employed to dispose of it. Difficulties being experienced with these traditional methods are then outlined, and the advantages offered by alternative methods of disposal based on the recycling of resources or the recovery of energy are described. A brief review then follows of some of the most important of these alternatives, with special emphasis on the acid hydrolysis and fermentation route. The analysis is not intended to be exhaustive by any means; rather, the aim is to locate the acid hydrolysis of refuse within the spectrum of refuse-to-energy conversion processes, and to highlight the advantages offered by this method.

2.2 Municipal Solid Waste Disposal in Britain

2.2.1 Quantities

Estimates of the total quantity of municipal waste currently being generated in Britain vary from 15 to over 20 million tonnes per year. The figure most generally agreed upon is 19 million tonnes (WMAC,1979; Cipfa,1982) made up of household waste, defined as the waste from private dwellings, schools and similar establishments, and commercial waste collected from shops, offices, and places of entertainment.

The reason for the large variation in the figures is lack of data: in England, the disposal of waste is in the hands of 46 Waste Disposal Authorities or WDAs (corresponding to the 45 counties and the Greater London Council) and not all the waste is weighed prior to disposal. However, a realisation of the importance (particularly to future waste disposal schemes) of reliable figures has led over the past few years to the gradual increase in the amount of waste that is actually weighed by the WDAs to 36% in 1979/1980 (Anon, "Figuring out rubbish",1981).

In London, where there have been radical changes in the waste disposal service since 1965, when the GLC assumed the responsibility for waste disposal from some 90 local authorities, much more detailed and frequent analyses are taken. Currently, some 98% of all domestic and commercial waste dealt with by the GLC is weighed before disposal (Millard,1981). The total weight amounts to over three million tonnes each year, and is increasing at the rate of two to three percent per year (Millard,1980).

Six other metropolitan areas - Greater Manchester, Merseyside, South Yorkshire, Tyne and Wear, West Midlands and West Yorkshire - together accounted for another four million tonnes of the municipal waste arising in 1980/81 (Cipfa,1982). Thus a total of seven million tonnes of refuse, or 38% of the total waste arising from waste collection authorities in England and Wales, was generated in areas of high population.

It is interesting to note that, on a per capita basis, there has been little change in the mass of waste generated in Britain in the last 50

years. In a presidential address to the Institute of Solid Wastes Management, Flintoff (1978) observed that between 1931 and 1976 the weight of domestic and commercial wastes generated per person per day in Britain rose by only 12%. In the same period, however, the volume of waste generated per person per day increased by a factor of 2.5.

This reflects the dramatic decrease in the average density of the waste from 342 kg/m^3 to 150 kg/m^3 (ibid). These trends are exemplified very vividly by the data given in Table 2.1 for the City of Birmingham, which show the change in the population, and in the mass and volume of refuse collected over the last 50 years. The decrease in the average density of the waste, and the corresponding increase in volume, arise from the change over the years in the nature and composition of typical refuse as collected from domestic, office and commercial premises. This subject is discussed in greater detail in the following section.

Table 2.1

Variation in refuse tonnage and density, City of Birmingham

Year	Population	Tonnes	Density (kg/m^3)	Volume (m^3)
1934	1 002 600	246 942	382.8	645 183
1960	1 090 500	318 280	252.5	1 260 550
1970	1 084 180	294 429	146.2	2 014 144

source: Bridgwater and Mumford, 1979, chap14.

2.2.2 Composition

The changes which have occured in the composition of municipal waste, leading to such an increase in its volume, are clearly indicated by the figures listed in Table 2.2, which shows the average refuse analysis for the City of Birmingham over the last 40 to 50 years. Particularly dramatic has been the drop in the dust and cinder content, reflecting the

replacement since the War (in most households) of open fires and kitchen boilers by oil and gas fired central heating. Equally remarkable has been the increase in the paper content, making it the largest single component to be found in municipal solid waste. The vegetable and putrescible fraction has also increased significantly, though not as much as paper.

Table 2.2

Analysis of refuse by weight (percent), City of Birmingham

Type of refuse	1934	1960	1970
Dust and cinder	75.03	49.72	15.91
Vegetable and putrescible	6.09	11.56	13.23
Paper and cardboard	7.71	20.48	51.42
Metal	3.31	6.44	6.41
Rags	1.51	1.39	2.42
Glass	1.15	7.26	6.45
Plastic	--	--	1.14
Unclassified debris	3.20	3.15	3.02
TOTAL	100.0	100.0	100.0

source: Bridgwater and Mumford, 1979, chap14.

The reason for these changes in the nature and composition of refuse is the change in life-style of the population, which has come about largely as a result of the improvement of general living standards. The increased use of disposable packaging, for example, which is a feature of the consumer society, is reflected in the enormous increase in the quantity of packaging material - paper, cardboard, plastic, glass or metal containers - found in domestic waste. It has recently been estimated that packaging accounts for about 30% of the weight of household rubbish (Anon, "Figuring out rubbish",1981).

Higher living standards and the increased use of convenience foods also account for the large quantity of vegetable and putrescible material found

in refuse. With more married women in employment, there is neither the time nor the economic incentive to produce economical home cooking. Moreover, concern about environmental pollution, which led to the declaration of smoke control areas, has made it illegal to burn rubbish on open fires (since refuse can hardly be classified as smokeless fuel) and this has resulted in the food and vegetable scraps finding their way into the rubbish bin, whereas in the past they would have been burned in the kitchen, together with any waste paper.

The trend towards greater quantities of paper and vegetable matter in waste may also be seen in the changes in the national average refuse composition figures over the last twenty years, as shown in Table 2.3.

Table 2.3

Analysis of refuse by weight (percent), Great Britain, 1963-1979

Type of refuse	1963	1970	1973	1976	1979
Dust and cinder	39	15	19	17	13
Vegetables and putrescibles	14	25	18	20	24
Paper	23	37	33	23	29
Metals	8	9	9	8	8
Textiles	3	2	3	4	4
Glass	8	9	10	9	10
Plastics	-	1	2	5	7
Unclassified	5	2	6	14	5
TOTAL	100	100	100	100	100

source: Cipfa, 1981.

It is interesting to compare the figures for 1970 in this Table with those in Table 2.2: there are obvious similarities, but significant differences too. The paper content, for example, of refuse in a big city is much higher than the national average, and so is the ratio of paper:vegetable/putrescibles. In fact, looking at the average refuse composition figures for a number of different towns or areas will

generally reveal a broad spread on either side of the national average. Many factors, such as size and location of the community, type of neighbourhood, as well as climatic conditions and the time of year have a bearing on the amount and kind of waste produced. This is important to keep in mind, as it is the actual quantity and composition of the refuse in a particular "catchment" area which must be taken into account when evaluating and comparing different methods of waste recovery or disposal.

2.3 Traditional Methods of Disposal

2.3.1 Landfilling

The traditional and still the cheapest way of disposing of waste, not only in Britain but in most countries, is by landfilling. In its simplest form, this involves deposition of waste in suitable excavations, such as disused quarries or gravel pits; in other cases, the waste can be used as a valuable fill for the reclamation of derelict land, for example in converting marshland to agricultural or leisure use.

Landfilling accounts for about 90% of the total refuse disposed of in Britain, and is carried out in an estimated 3000 sites of widely ranging size and shape (Osmond,1980). Initially, landfill sites were situated close to urban and industrial areas, but as these areas have become more densely populated, and the landfill sites exhausted, it has become increasingly difficult to find suitable alternatives near at hand. As a result, more and more cities are turning to the use of transfer stations and long- or short-distance haulage systems to transport their refuse to disposal sites sometimes many miles outside the city limits.

The need for a transfer station arises when the distance from the last pick-up point to the landfill site exceeds a certain limit (which may be calculated using operational research techniques). It is uneconomical for a collection vehicle, equipped with a compacting mechanism and carrying a crew of three or four persons for rear-end loading, to undertake long trips to distant landfill sites. Specially designed lorries, trains or barges, which can carry larger payloads and are not

burdened with compaction equipment or collection crews, are used for this operation instead. The transfer station is a point at which refuse is transferred from local collection vehicles to the long distance haulage transport.

At its simplest, a transfer station need only be a storage bunker, into which collection vehicles discharge their loads, and from which bulk transporters may be loaded. Most modern transfer stations, however, include facilities for shredding or pulverising the waste and compacting it, thereby reducing its volume and hence the number of trips required to the landfill site. Shredding the waste prior to tipping or landfilling is also claimed to have many benefits in terms of improved tip stabilisation and land reclamation, and there is a strong body of opinion which advocates that it should be a mandatory requirement when giving planning consent for new landfill sites.

The extent of the difficulty being experienced in finding landfill sites near to centres of waste generation may be appreciated from the fact that in twenty non-metropolitan counties in England, at least some refuse was processed through bulk transfer stations in 1980/81 (Cipfa,1982). As might be expected, the problem is at its worst in London, where the GLC operates a scheme in conjunction with British Rail to transport some 600 000 tonnes of waste each year in totally enclosed containers to large-scale landfill sites 50 miles or more away, in Oxfordshire, Bedfordsire and Buckinghamshire. A roughly similar amount is transferred to barges and taken down the Thames to the Essex marshes (also a distance of some 50 miles) while a further 1.5 million tonnes is transported by road to closer landfill sites (Millard,1980,1981).

2.3.2 Incineration

Another significant method of waste disposal in Britain is incineration, which accounts for about 10% of the refuse that is handled by the Waste Disposal Authorities (Cipfa,1982). In a properly designed and operated incinerator, waste material may be reduced by up to 90% in volume, and up to 60% in weight, and the residue, being ash, is much more easily and cheaply transported and disposed of than the original waste.

Moreover, it has the advantage of being sterile - thus, it can often be used as a safe and stable construction material in road making and other building projects.

Incineration has a long history in Britain. The world's first large municipal incinerator was constructed in Nottingham in 1874 (Vesilind and Rimer,1981,chap8). By the 1960s many urban councils, unable to find suitable landfill sites within their areas, had turned to incineration as a means of disposing of their refuse. Now that the responsibility for waste disposal has been transferred from district councils to the counties, and urban wastes may be disposed of outside district boundaries, the need for incinerators has been correspondingly reduced.

Incineration need not be used only as a means of reducing the volume or weight of refuse requiring eventual landfilling, however: the heat produced by burning the refuse may be recovered in a boiler and put to good use. This is called recuperative incineration, and is widely practiced on the continent, in France and Germany especially (Marx,1976). In Britain, however, of 48 refuse incinerators operating in 1978, only four were being used for energy recovery, together burning a total of 900 000 tonnes of municipal solid waste per year (WMAC,1979). As far as is known, these incinerators are still in operation. Those at Sheffield and Nottingham produce steam for district heating, while that at Coventry produces heat for an adjacent factory, and power for in plant use.

Only one incinerator in Britain, at Edmonton in London, raises steam for the production of electricity. It is the largest incinerator in the country, and was specifically designed for heat recovery from domestic refuse. Many initial difficulties were experienced after the installation of the plant in 1971, but currently the incinerator burns 400 000 tonnes of London's waste each year, and in 1980 exported 160 million units of electricity, giving the GLC an income of £2.5 million (Millard,1981).

2.3.3 Composting

Composting of municipal refuse is carried out on a small scale in Britain. Nitrogenous compounds are almost non-existent in British refuse, resulting in a very high carbon:nitrogen ratio in compost derived from it. This means that its fertiliser content is minimal. Leicester County Council have overcome this problem by adding sewerage sludge to the compost, which increases the nitrogen content. In this way, they have obtained reasonable sales (PT 272,p31). On a national basis, however, this method accounts for less than one percent of municipal solid waste disposed. Only the organic fraction is suitable for composting, and 50 to 60% of the original volume remains for disposal by some other method.

2.4 Reasons for Seeking Alternatives

2.4.1 Cost and other problems with traditional methods

For many years, the general policy for waste disposal could perhaps have best been summed up in the phrase, "out of sight, out of mind". Waste materials were considered to have no value, and to be fit only for disposal by the cheapest possible method.

Nowadays, concern about environmental impact has led to much tighter controls on the disposal of wastes. The traditional method of disposal to land is now subject to a strict code of practice (DoE,1971) which has inevitably resulted in increasing expenditure in the management and operation of existing landfill sites, and in increasing difficulty in finding and developing new, environmentally acceptable sites as those near to waste generation centres are used up.

There is a school of thought which claims that, as the volume of mineral excavations each year is greater than the volume of refuse generated, there will never be a shortage of landfill sites. It might not be appreciated, however, that "... a lot of the mineral excavation is away from populated areas, below water tables, close to public water supplies or in areas of outstanding beauty ... such sites are thus totally unsuitable

on grounds of environmental amenity and/or geological conditions for refuse landfill ..." (Porteous,1981,chap1).

The problem of finding suitable sites available for landfilling is highlighted by the continued trend away from untreated landfill, and the increasing use of pulverisation and incineration processes, in the metropolitan areas especially (Cipfa,1982). It is reflected also in the spiralling cost of refuse disposal in recent years, which has been substantially in excess of the general inflation level. In 1979/80 the net expenditure on waste disposal in England and Wales was 31% higher than in the previous year, compared with a rate of inflation of around 19% (Higginson,1981); in 1980/81 there was a further increase of 24%, compared with the general inflation level of around 13% (Cipfa,1982).

Table 2.4

Typical waste transfer and disposal costs - London, 1979

transport	distance to landfill from transfer station km	costs in £s per tonne			
		transfer	transport	landfill	total
road	50	3.25	2.00	1.50	6.75
rail	80	3.50	2.25	1.75	7.50
river	80	4.00	2.30	2.20	8.50

source: Millard, 1981.

The GLC, which has to transport its waste particularly long distances, has special problems. Table 2.4 shows how much is added to the cost of disposal of a tonne of refuse when it has first to pass through a bulk transfer station and be transported a significant distance by road, rail or river. Other metropolitan areas are begining to face the same problems: in October 1981, a new refuse treatment plant was officially opened in North Manchester to pulverise and transfer 600 tonnes per day of

waste to containerised rail transport. The plant cost £7 million, and was the first of a series of rail-linked plants that are planned for Greater Manchester. Two similar plants are already under construction (Anon, "Manchester's new £7 million plant",1981). Over the whole country, a total of £12 million was laid out in capital expenditure on bulk transfer processes in 1980/81 (Cipfa,1982).

The comparative costs of various methods of refuse treatment and disposal in Britain are given in Table 2.5 for the year 1980/81. The high cost of shredding or pulverising refuse prior to landfilling is apparent. Costs are likely to rise further as landfill sites become harder to acquire, transportation distances become greater, and pollution control standards are more vigourously enforced. If some form of pretreatment like shredding or pulverisation does become mandatory for better tip control, another step change would be added to the cost of this method of refuse disposal.

It was thought for a time, especially in the late 1960s and early 1970s, that incineration would provide the answer to most of Britain's refuse disposal problems. It is true that in large urban areas, where landfill is remote and expensive, incineration offers the advantage of high volume reduction of solid waste, and a sterile char. But incineration is not without its problems, either; and the major one is economics.

The capital cost of incineration equipment is very high, especially if heat recovery is contemplated. Conversion of the heat produced to electricity is probably the most expensive option of all. At Edmonton, in London, where 400 000 tonnes of refuse is burned each year and 160 million units of electricity exported, waste disposal still costs around £11.50 per tonne, even after allowing for income from the sale of electricity - and this in a plant that was constructed in the late 1960s, and whose capital cost (£13 million) has presumably been written off. The capital cost of a new Edmonton at today's prices would be over £50 million, the principal reason for the GLC not building any more incinerators nor having any plans to do so (Millard,1981).

Table 2.5

Methods of waste treatment and disposal - comparative net costs per tonne

method of treatment	£ per tonne - net of capital charges					
	non metro-politan counties	metro-politan counties	GLC	rural districts	urban districts	all authorities
landfill untreated	2.46	2.45	9.28	2.76	1.44	2.47
landfill after shredding/ pulverisation	10.86	8.46	16.21	--	--	11.36
contractors and other WDAs and agents	5.99	4.65	10.72	7.67	2.91	8.05
direct incineration	8.44	12.95	8.72	--	17.55	10.71
separation and incineration	7.83	22.26	--	--	--	16.70
other methods	16.01	9.76	--	--	--	12.02
ALL METHODS	4.72	8.04	12.24	4.28	2.23	6.17

Other difficulties with heat recovery systems lie in the distribution, availability and grade of heat, and the size and proximity of customers. Porteous (1978) has examined the costs of recuperative incineration in all its forms, and concluded that the excess capital expenditure (over non-recuperative incineration) is not cost effective where heat is sold to separate businesses or premises, unless the municipality is prepared to subsidise the cost of the operation. Other ways of utilising the fuel potential of refuse are now being explored in Britain.

2.4.2 Advantages of recycling and energy conversion

While it is becoming more difficult and expensive to dispose safely of municipal solid waste, its potential as an alternative source of raw materials or energy (or both) is becoming increasingly appreciated. Ecologists had been warning for years that the earth's resources are not inexhaustible, but it was not until the publication of "The Limits to Growth" (Meadows et al,1972) and the oil crisis of 1973 that public awareness was jolted into the realisation that the rate of extraction of fuels and materials from the earth's surface could not continue unchecked without the reserves becoming rapidly depleted.

Since then, the explosion in the cost of oil and gas, and the continued escalation in the prices of the major raw materials has lent added urgency to the search for renewable or natural energy sources, and reinforced the awareness of the need for resource and energy conservation. Municipal solid waste, once thought of only in terms of being a nuisance to dispose of, is beginning to be regarded as a mine of valuable raw materials which should be worked, as well as a potential fuel which may be harnessed in a variety of different ways.

Recycling the materials found in refuse instead of discarding them offers many advantages. First of all (and especially with regard to metals) the rate of extraction of primary raw materials is slowed down, and since these resources are non-replenishable, the life-period of the reserves is considerably extended. Secondly, as these materials are usually imported, recovering them from refuse for reuse within the economy helps to contribute towards the balance of payments, and reduces the

nation's dependence on foreign suppliers. Thirdly, considerable savings in energy may be made by recovering materials from refuse and reprocessing them into new products, compared with producing equivalent products from virgin raw materials: Table 2.6 shows how between 30 and 70% of the energy required to produce certain materials may be saved in this way. Finally, by reducing the quantity of material going to waste, the problems of eventual disposal discussed above are minimised.

Table 2.6

Energy required to produce equivalent products from primary raw materials and domestic wastes

	Energy required (kW/tonne)			
	primary production	from domestic waste	difference	energy conserved %
paper	5 712	4 198	1 514	27
glass	5 060	2 868	2 192	43
crude steel	4 146	1 464	2 682	64
aluminium	60 945	19 595	41 350	68

source: Turowski, 1978.

In addition to, or as an alternative to, recycling some of the materials to be found in refuse, the waste may be used in whole or in part as a source of energy. Refuse contains, besides metals and glass, a mixture of combustible materials which may be burned or used as feedstock for conversion to some other form of energy. Recuperative incineration, for example, has already been mentioned above as a way in which the fuel value of refuse may be recovered.

The Arab boycott of 1973 highlighted the vulnerability of Western economies to disruptions in their supply of imported oil. But closer analysis showed the situation to be even more alarming - the world's oil reserves are being used up so quickly that even after allowing for conservation and the discovery of new wells, they will be completely exhausted by the middle of the next century (Warman,1980). Coal will provide a temporary breathing space, but in the really long term Britain like the rest of the world will come to depend almost exclusively on renewable sources of energy (Lacey,1976).

As an alternative to conventional fuels, municipal solid waste falls into the category of biomass, which may be defined as all forms of plant matter containing stored solar energy. On a weight or volume basis the combustibles in refuse are made up primarily of the paper and vegetable fractions, which in turn are derived from products of agriculture and forestry. Unlike coal and oil, which take millions of years to form beneath the earth's surface, these are a perpetually renewed source of energy and matter.

Typically, the calorific value of crude refuse in Britain is in the range 9000 to 11 000 kJ/kg; thus the total annual arisings of about 19 million tonnes of refuse have a heat content equivalent to six million tonnes of industrial coal (Porteous,1981,chap2). Naturally, it would not be possible to recover all this energy - it would probably be feasible to process the waste from the largest communities only - but what could be made available would make a small but significant contribution to Britain's energy requirements.

2.5 Alternative Methods of Municipal Solid Waste Disposal

2.5.1 Materials reclamation

As suggested above, alternative waste treatment methods may, broadly speaking, be divided into two categories, materials reclamation and energy recovery, though some processes may include both of these alternatives. Perhaps the simplest method of recovering materials from refuse (in

conception, at least) is "separation at source", in which householders sort out different items from the rest of household waste; these items are then collected separately and returned to the relevant industry for recycling. Trial schemes, on a voluntary basis, have been operated in Sweden (Von Heidenstam,1980), other European countries (Hammond, 1975) and in the U.S.A. (Duncan,1976) for the recovery of paper, glass, metal and plastics, but attitude and lack of incentive make such schemes difficult to operate and uneconomical.

As an alternative, automatic sorting processes have now been developed for separating the components of mixed domestic refuse. These processes are based largely on methods derived from the mining industry, and include pulverisation, screening and pneumatic sorting for the initial selection and separation of the light-weight components (paper and film plastics); and wet sorting, and electromagnetic, electrostatic, optical and cryogenic systems for the separation of glass and metals (Bonomo,1980).

In continental Europe and Scandinavia, the emphasis in these sorting processes is on paper recovery, since many countries anticipate future fibre shortages. Consequently, much of the research and development activity has focussed on removing contraries and dirt from the recovered paper so that it can meet specifications for reuse in papermaking plants (Alter and Dunn,1980,chap4). There is also considerable interest in the recovery of the organic putrescible material for the production of compost or dried animal feed.

In Britain, on the other hand, as in the United States, the development of automatic refuse sorting proceses is directed at the production of refuse derived fuel (RDF) in both loose and pelletised forms. Several schemes are being pursued in Britain, both in the public and private sectors. The plants at Doncaster and Byker are perhaps the best known, and were constructed with financial support from the Department of the Environment. The recovery of energy from refuse in the form of refuse derived fuel is described in section 2.5.2. below, so the discussion here will be limited to the mechanical sorting and materials recovery aspects of the Doncaster plant. This is of particular relevance to the present work, as air-classified lights from the Doncaster plant were actually used

in the hydrolysis experiments described in Chapter 5 as being representative of a "typical" refuse feedstock available for a hydrolysis process.

The design of the Doncaster plant was based on research and development work carried out at the Department of Industry's Warren Springs Laboratory in Stevenage. A flowsheet of the plant appears in Figure 2.1. Incoming refuse is screened prior to size reduction, in order to minimise the costly shredding operation to that part of the feed that will produce the RDF product. A rotary trommel selects material between 50 and 200 mm in size; this material is magnetically separated to remove ferrous metals, and sent to the air-classifier. The air-classified lights are shredded in a knife mill and made into pellets: this is the RDF product. The heavies undergo dense medium separation in brine, followed by optical sorting, to recover glass.

Three other size fractions are produced by the primary screen. Fine material (<13 mm) is discarded. Oversize (>200 mm) is shredded and air-classified for paper recovery. Another middling fraction (>13 mm <50 mm) is magnetically separated and subjected to dense medium separation to recover ferrous metals and glass.

The Doncaster plant was officially opened in December 1979. At full design capacity, it is expected to treat 62 500 tonnes of material annually and recover 3125 tonnes of glass, 3125 tonnes of magnetic metals, 1250 tonnes of paper (secondary fibre) and 10 000 tonnes of RDF (Kut and Hare,1981,chap6). The remainder of the incoming refuse will still require disposal, but volume reduction is expected to be about 70% (Mahoney, 1980).

The Doncaster process differs from that at Byker in that it is essentially multi-resource recovery which is being attempted, whereas the Byker plant is designed to recover RDF and ferrous metals only. The Byker plant itself displaced a smaller plant, designed and operated by Material Recovery Ltd, which recovered tin and steel from shredded refuse at a transfer station in Newcastle-upon-Tyne. MRL have now opened a new and more advanced plant at Staffordshire County Council's incinerator station at Stoke-on-Trent and hope to recover 9000 tonnes of used tin cans from

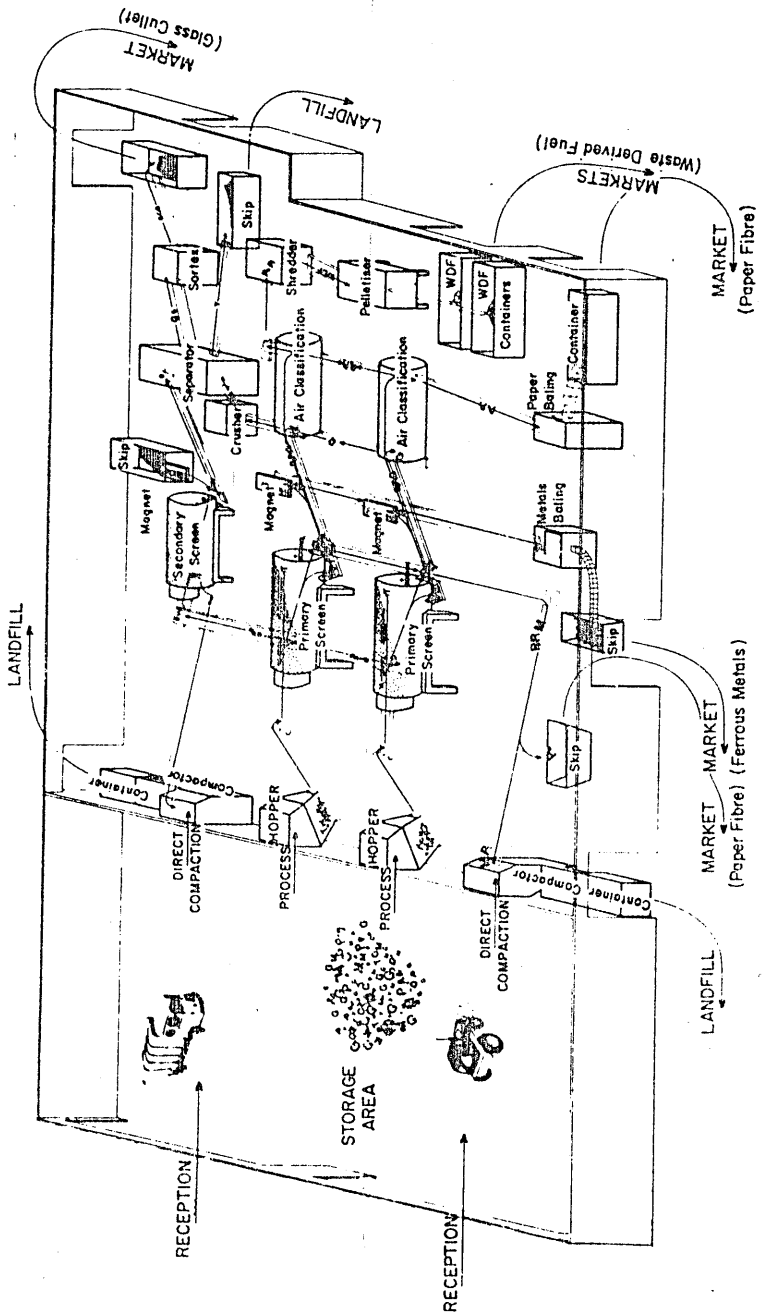

Figure 2.1. Flowsheet of Doncaster RDF plant (source: Porteous, 1981).

the 120 000 tonnes of refuse which pass through the incinerator each year (Robinson,1980).

2.5.2 Refuse derived fuels

Refuse derived fuel or RDF is a general term to describe a fuel produced from refuse, by some form of size reduction and sorting process. The fuel may be in a loose or pelletised form, and may be burned on its own or as a supplement to conventional fuels.

Imperial Metal Industries of Witton in Birmingham have been operating a project since 1976 to burn 50 000 tonnes of refuse per year as a supplement to coal in two converted water-tube chain-grate boilers. Refuse delivered to the plant by the West Midlands County Council is pulverised and passed over a magnetic separator before entering the boilers. Since 2.5 tonnes of unscreened refuse have roughly the same heat content as one tonne of coal, considerable fuel savings are made in this way (Porteous,1981,chap4). A flowsheet of this plant appears in Figure 2.2.

Another scheme, operated by the Blue Circle Cement Company at their Westbury plant in Wiltshire uses refuse as a partial fuel replacement in a rotary cement kiln. The plant takes 60 000 to 80 000 tonnes of refuse per year from the Wiltshire County Council; the process involves two-stage pulverisation to <50 mm, followed by ferrous metal extraction, prior to firing in the kiln (see Figure 2.3). Almost total disposal of refuse is achieved in the process, as the residue from combustion is mixed in with the cement clinker (Porteous,1981,chap4).

There would appear to be considerable potential for other selected industrial premises to install purpose designed heat recovery systems, or to convert existing systems, to burn refuse in order to raise the energy requirements of processes carried out on those or adjacent premises. Refuse arising on site would be burned in the first instance (either on its own or in conjunction with another fuel) and additional refuse could be imported from nearby industrial premises or WDAs as required. This would result in substantial savings on conventional fuels and on waste disposal costs (Temple-Pediani,1981).

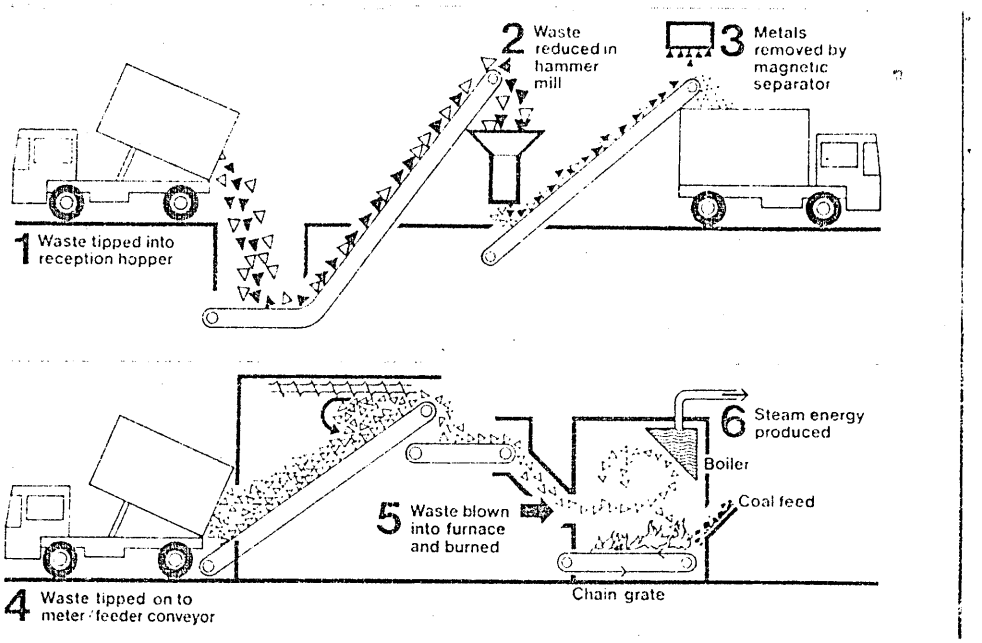

Figure 2.2. Flowsheet of IMI Witton refuse burning scheme (source: WMAC, 1979).

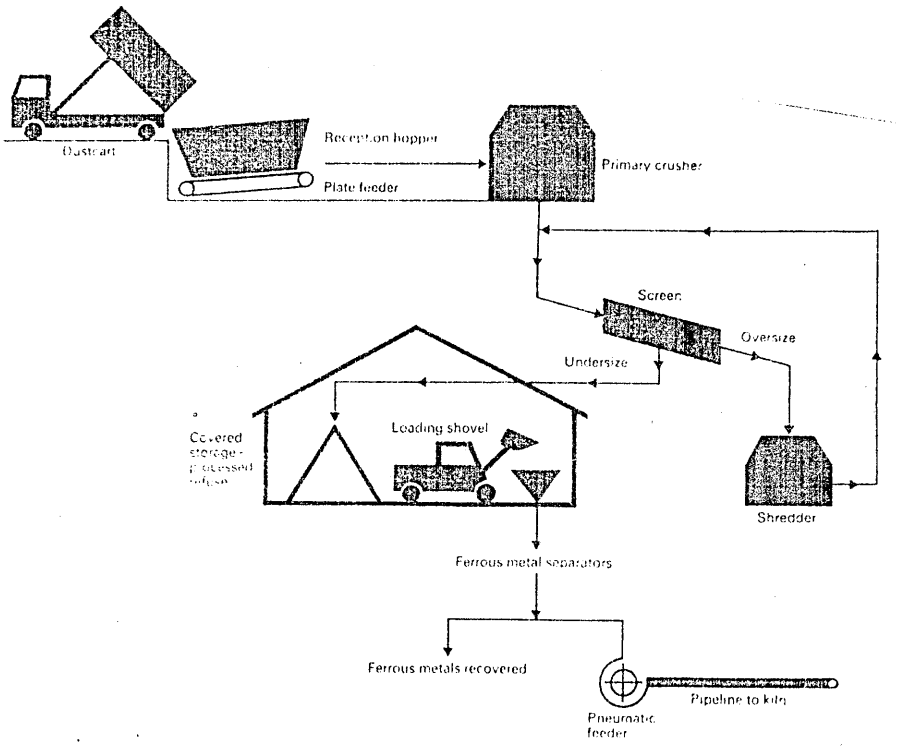

Figure 2.3. Flowsheet of Blue Circle Cement refuse burning scheme (source: WMAC,1979).

This philosophy of waste management requires minimum processing of crude refuse, and typically allows the combustion of about 60% of the tonnage normally received by the WDAs. An alternative philosophy, exemplified by the Byker and Doncaster recycling plants and very much preferred in the United States is to process the refuse further into a higher grade fuel in a form which may be easily handled, stored, and transported. The RDF pellets produced at Doncaster contain practically only the paper content of the refuse and some plastics: other combustibles, such as putrescibles and rags, are separated out during the sorting process. The pellets have a high calorific value of about 15 000 kJ/kg, or approximately half that of coal, and contain about 16% of the raw refuse which entered the plant (Mahoney,1980).

It is interesting to note briefly in comparison that the RDF pellets produced at Byker contain about 30% of the weight of the incoming refuse. This seeming anomaly is a result of the difference in composition between the refuse feeds to the two plants. Doncaster is in a domestic coal burning area, and has a higher fines and lower paper and board content in its refuse than that at Byker. The difference in RDF yield is a good illustration of the effect of location and local conditions on the performance of refuse treatment or recovery plants (Porteous, 1981,chap9).

The RDF plants at Doncaster and Byker were built to evaluate mechanical sorting with RDF recovery as a waste disposal option in Britain. At present, the only real problem would appear to be market resistance to the product. On the basis of energy content, RDF pellets ought to command a price of £22 per tonne, which is half the price of coal. Economic calculations show that at a selling price of £15 per tonne, RDF would still be cost-effective, i.e. be competitive with transfer station and haulage disposal costs (Porteous, 1981,chap9). But indications are that as little as £10 per tonne is the maximum price that some industries are prepared to pay, owing to a conservative approach to this new form of fuel.

The problem would appear to be largely psychological. Some industries still regard burning refuse as unsavoury. Time, and the successful operation of the experimental plants, could well allay the doubts of potential users of RDF. Long-term considerations certainly point towards

the adoption of more such schemes.

2.5.3 Pyrolysis

Pyrolysis is the physical and chemical decomposition of organic matter brought about by the action of heat in an oxygen-free or oxygen-deficient atmosphere. The result is not combustion or oxidation but a complex series of chemical reactions which produces a mixture of gaseous, liquid and solid residues which may be used either as fuel or raw materials for the chemical industry.

The pyrolysis of refuse is usually carried out in a retort at temperatures between 500 and 1000°C. The products are a mixture of gases (chiefly hydrogen, carbon monoxide and methane), liquids (tars, oils and an aqueous condensate) and a solid char, whose combined energy content exceeds the energy consumed in the process. The ability to separate these materials, and to store and transport the fuel components, gives pyrolysis a potential edge over straight incineration of refuse.

The organic fraction of refuse which undergoes pyrolysis consists mainly of the paper, plastics, putrescibles and rags, and may conveniently be approximated to cellulose in chemical composition. Cellulose can in fact be treated as the basic raw material for the whole range of refuse-to-energy processes, of which pyrolysis is but one. Inert materials such as glass and metals are usually removed from the refuse prior to pyrolysis, and the remaining organics shredded or pulverised, and sometimes air-classified.

Descriptions of various refuse pyrolysis processes are beginning to appear in standard texts on solid waste treatment and disposal (e.g. Porteous,1981,chap7; Vesilind and Rimer, 1981, chap9; Bridgwater and Mumford, 1979, chap17) but very few commercial plants have been built and they are mostly in North America. In Britain, work on pyrolysis at present is centred mainly on used tyres.

Current problems with refuse pyrolysis are mainly connected with economics and pollution control. Like incineration, pyrolysis is very capital intensive, and is unlikely to be adopted by WDAs in the near future

as a refuse disposal alternative. In the longer term, however, it may well become more competitive with other refuse-to-energy conversion techniques.

2.5.4 Anaerobic digestion

Another of the alternatives being pursued as a means of converting the organic material in municipal solid waste into a useful fuel is anaerobic digestion. This process is commonly used in sewage treatment and results in the decomposition of organic matter and the production of a gas containing a high proportion of methane. The gas has a calorific value of about 23000 kJ/m^3 (Palz and Chartier,1980) and is usually used to run engines or gas turbines to provide the heat and power requirements of the sewage plant itself; alternatively, it may be purified to pipeline quality methane gas for sale to other users.

Anaerobic digestion is a biological degradation in which complex organic molecules are broken down by various species of bacteria and other micro-organisms. It is usually carried out in closed, heated and stirred cylindrical vessels, with continuous addition of fresh sludge and continuous removal of gas and residual solids. Since the predominant component of typical solid waste is cellulose, the basic bioconversion reaction is

$$\underset{\text{cellulose}}{C_6H_{10}O_5} + H_2O \longrightarrow 3CO_2 + \underset{\text{methane}}{3CH_4} + \text{heat}$$

Typically (in sewage treatment) the solids are reduced by about 40% in weight or 65% in volume, and in the process about 0.5 m^3 of gas is produced per kg of organic material entering the digester (Bridgwater and Mumford,1979,chap7).

Because of the potential of the process for producing energy, many other organic wastes have been evaluated in recent years as possible substrates for anaerobic digestion, including screened and sorted municipal refuse. The organic fraction of refuse (paper and vegetable matter) is composed basically of the same compounds (carbohydrates,

proteins and fats) as sewage sludge, and undergoes anaerobic digestion in the same way, although certain deficient nutrients have to be supplied, usually by the addition of limited quantities of sewage sludge.

Pfeffer and Liebman (1976) were among the first to study the anaerobic digestion of shredded refuse in the laboratory, and determined the rate and quantity of gas production at various operating temperatures and retention times. Subsequent work has evaluated the effect of pH and solids loading on the process. More recently, Chase and Singletary (1981) have investigated RDF production as a pretreatment step to anaerobic digestion of municipal solid waste, and Ghosh et al (1980) have carried out digestion trials on blends of other biomass species together with municipal solid waste and sewage sludge in an effort to improve the economic feasibility of the process.

To date, however, attempts at conventional liquid-slurry digestion of organic refuse have not reached the commercial stage. The largest test facility being operated in the United States, the 100 tonne/day RefCOM plant at Pompano Beach, Florida, has encountered many problems: yields of methane are low at less than 0.06 m^3/kg (1 ft^3/lb) of feed (Klass,1980), the proportion of solids remaining for disposal is high, and a variety of mechanical problems has resulted in numerous delays in the experimental programme. Much more work is required before anaerobic digestion might become a viable proposition as a refuse disposal method.

2.5.5 Hydrolysis and fermentation

The production of ethanol by fermentation is one of the oldest processes known to man. All beverage alcohol is made in this way, and until the late 1920s industrial alcohol too was produced almost exclusively by fermentation. Nowadays, industrial ethanol is produced mainly by the hydration of ethylene, obtained from oil or natural gas; but there was a time when things were otherwise, and ethylene was obtained by the dehydration of ethanol, as the first step in the production of many of the chemicals presently derived from oil (Jullander, 1975).

At present, in industry, ethanol is used primarily as a solvent, and as an intermediate in the organic chemical industry; but it is also being

used as a fuel, to replace petrol either wholly or partially in internal combustion engines. This last application has attracted much attention in recent years, and many countries (Brazil is a well-known example) have instituted national programmes for the production of ethanol in large quantities to lessen their dependence on imported oil.

Ethanol-based chemicals or "ethyl-chemicals" are also enjoying a return to favour - and among the ethyl-chemicals now in production in Brazil are butanol and octanol, ether, glycol ethers, butadiene, and halogen derivatives (Othmer,1981). The revival of interest in this field is evidenced by the number of papers which have appeared in the literature in recent years outlining a wide range of possible reaction schemes for the production of chemicals from ethanol (e.g. Brenner, Rugg and Rogers,1977; Humphrey,1975; Edwards,1975; Goldstein,1975), and ethanol production by fermentation is likely to become ever more important as the prices of ethylene and other petrochemicals rise, reflecting the increasing scarcity and price of crude oil (Huff,1981).

The raw materials for producing ethanol by fermentation are various agricultural products and residues, which may be divided into three categories, according to their dominant chemical characteristic:

(a) Sacchariferous materials, such as sugar cane, sugar beet, fruits and similar materials, which contain natural sugars.

(b) Amylaceous materials, such as wheat, maize, potatoes, rice, and other grains and tubers, which contain starch.

(c) Cellulosic materials, such as wood and crop residues (bagasse, wheat straw, maize stalks, etc) which contain cellulose.

Fermentation itself is a biochemical process, in which sugars are converted by the action of yeasts into ethanol and carbon dioxide. The stoichiometric equation may be expressed as

$$C_6H_{12}O_6 \text{ ------> } 2CO_2 + 2C_2H_5OH$$

As sacchariferous materials already contain natural sugars, fermentation can proceed directly. But with amylaceous or cellulosic materials, it is necessary to precede the fermentation by a process which will convert the starch or cellulose into fermentable sugars. This is the process of hydrolysis. It involves the depolymerization of starch or cellulose by the addition of water. Starch hydrolysis proceeds relatively easily, by cooking the starchy material and treating it with various plant and animal enzymes. Cellulose hydrolysis is more difficult, and requires the use of heat and pressure and the aid of an acid catalyst to break down the cellulose molecule. Cellulose hydrolysis may also be carried out enzymatically, but then requires intense physical or chemical pretreatment to make the cellulose molecule available for reaction (this point is discussed in more detail in Chapter 3).

It has already been noted above that the organic material in refuse contains a high proportion of cellulose, found chiefly in the paper and paper products, which constitute the largest single component of typical refuse. This cellulose may be converted to ethanol by conventional fermentation technology, provided it is first separated from the remainder of the waste, and hydrolysed to fermentable sugars. The separation may be carried out by the same sort of process that is used to produce refuse derived fuel; or, alternatively, some sort of source separation might be considered, in which the public is asked to keep paper separate from the rest of their waste. But the hydrolysis step is still under development, despite a great deal of research that has been carried out, particularly in the U.S.A., during the last ten to fifteen years.

A number of alternative schemes are being investigated for the conversion of cellulose to fermentable sugars; these are generally based on the use of either dilute acid or cellulolytic enzymes to carry out the hydrolysis, though some processes incorporate the use of both these agents. Several methods of pretreating the cellulose by various chemical or physical means, in order to facilitate the hydrolysis reaction, are also being studied. Enzymatic hydrolysis and the various methods of pretreatment that have been suggested, are reviewed briefly in sections 3.6 and 3.7 below: the dilute acid hydrolysis of cellulose, and of refuse, is the subject of the next section, and of the rest of this thesis.

2.6 Potential of Acid Hydrolysis as a Refuse Disposal Method

As outlined above, the acid hydrolysis of cellulosic material in refuse is aimed at converting the cellulose into sugar, which may be fermented to ethanol. Cellulose is converted quantitatively into glucose on hydrolysis with acids, according to the equation

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{glucose}}{nC_6H_{12}O_6}$$

The acid acts as a catalyst in the depolymerisation of the cellulose molecule, but the process must be operated at high temperature and pressure for the reaction to proceed at any appreciable rate.

The process has found commercial application in the past, from as long ago as during the First World War (see section 3.3) for the production of ethanol from wood residues.The earliest plants were in the United States, but the technology was later developed in Germany, and then in Russia, where there are still "tens of plants" processing wood and agricultural wastes by acid hydrolysis to this day (Karlivan,1980). The traditional technology uses a semi-batch "percolation" technique, in which dilute acid flows continuously through a stationary bed of solid, at temperatures of 150° to 180°C and reaction times of up to three hours (Wenzl,1970,chap4). A major problem which percolation hydrolysis tries to circumvent (by swift removal of the hydrolysates from the reaction zone) is simultaneous decomposition of glucose, which is favoured by the same reaction conditions of high temperature and low pH which accelerate the cellulose hydrolysis reaction.

As an alternative, there are processes using concentrated acids which depend on disrupting the cellulose structure by solution or swelling in the acid: the cellulose is then hydrolysed rapidly at temperatures low enough to avoid degradation of the glucose product. The Bergius process used superconcentrated hydrochloric acid (up to 41%) at ambient temperatures or below; the Japanese Hokkaido process used 80% sulphuric acid at room temperature (Goldstein,1980). Other processes, such as the Prodor process, used HCl gas (Funk,1975).

The problem with these processes is that they require higher capital costs for corrosion resistant equipment, and incur higher operating costs associated with acid recovery and loss. Economic considerations dictate that acid recovery is essential, but the cost of doing this is usually prohibitive. As far as is known, there are no commercial plants still in existence using concentrated acid hydrolysis, and all the present work into cellulose hydrolysis is based on the use of dilute acids (or enzymes).

Although the end-product of cellulose hydrolysis has usually been ethanol, other products may also be obtained from cellulose hydrolysates. In Russia today, for example, as in Germany during the last War, protein shortages have led to the glucose in the hydrolysates being used instead for the production of fodder yeast (Saeman,1980). This process was also the subject of an extensive investigation in the United States (Peterson, Snell and Frazier,1945); Torula utilis and Candida tropicalis were found to be satisfactory organisms, and yields (calculated as dry yeast) of 35 to 40% of the total reducing sugar in wood hydrolysates were obtained regularly. About 90% of the apparent reducing sugar was fermented.

Other routes to alternative products from cellulose hydrolysis may also begin with glucose. Veal and Whalley (1981), in a recent article written especially for the U.K., explored the applications and markets for some of the organic chemicals which might be made from the products of cellulose hydrolysis. Acetone, butanol, and citric, gluconic, itaconic and lactic acids were all identified as possible glucose fermentation products, while levulinic acid and hydroxymethylfurfural could be produced by chemical reaction. These last two chemicals are in fact the products of glucose decomposition on exposure to hot mineral acid, and as such would be expected to be found in all commercial cellulose hydrolysates. Hydroxymethylfurfural is produced first, but is not very stable, and is readily degraded to levulinic acid (Harris,1975). Both these chemicals are highly reactive and multifunctional and, if separated from hydrolysates, could be valuable starting materials for organic synthesis (Newth,1951; Leonard,1956; Harris, Saeman and Locke, 1963).

There are other chemicals which are usually found in the hydrolysates of cellulosic materials: the most important is furfural, which is derived from hemicellulose, another polysaccharide which is always found in close association with cellulose (see section 3.2.1). Hemicellulose is much more readily hydrolysed to simple sugars (pentoses and hexoses) than cellulose is to glucose: thus in over 40 Soviet wood hydrolysis plants, a two-stage process is employed, involving initial removal of the hemicellulose fraction at relatively low temperatures (80° to 120°C) followed by cellulose hydrolysis at higher temperatures (about 180°C) (Humphrey,1979). Furfural is produced from the pentoses contained in hemicellulose hydrolysates, and is used as a selective solvent when making lubricating oils or for conversion to furfuryl alcohol, for use in making foundry resins (Veal and Whalley,1981).

The third major constituent of cellulosic materials, lignin (see also section 3.2.1), does not react under the conditions of dilute (or concentrated) acid hydrolysis, but remains unchanged at the end of the process. It may be recovered, and used as a process fuel (lignin represents approximately 50% of the available combustible energy in naturally occuring sources of cellulose (Humphrey,1979)) or converted by various hydrogenation and hydrogenolysis techniques into a range of phenolic products (Goldstein,1975). The recovery of all these chemicals need not, of course, necessarily be the aim of a process designed to hydrolyse the cellulosic content of refuse: but it is one of the advantages of acid hydrolysis as a waste disposal method that such a wide variety of useful products may be obtained from the process.

Ultimately, however, the crucial step in developing any new hydrolysis technology is in the hydrolysis reaction itself, and in the optimisation of cellulose conversion to glucose. In his original proposal to treat municipal solid waste by an acid hydrolysis process, Porteous (1967) outlined a scheme which included a significant break from traditional hydrolysis practice, by recommending the use of a continuous plug-flow reactor, to be operated at higher temperatures than previously used in cellulose hydrolysis (220° to 230°C) and very much smaller contact times

(of the order of a minute). _1] Porteous suggested that under these new conditions, yields of glucose comparable to those obtained in the traditional wood hydrolysis processes, would be realised. The advantages would lie in the considerable savings that could be made in capital equipment (the plug flow reactor would be roughly 200 times smaller than the equivalent batch or semibatch reactor handling the same throughput (Porteous, 1976)) and in the fact that percolation hydrolysis would probably be impossible with fibrous substrates such as waste paper or sorted refuse, anyway. They would tend to compact into a tight impermeable mat which would prevent the acid from percolating through the bed (Grethlein,1978).

In his design of a refuse hydrolysis plant, Porteous (1967) envisaged the extraction of the cellulosic part of the refuse by pulverisation followed by flotation separation: the lighter fraction, containing mostly cellulosic materials, would be shredded and fed into the hydrolysis reactor. At the end of the reaction, the product would be flash cooled, neutralised with lime and filtered, the filtrate proceeding to fermentation and distillation to 95% ethanol. Nowadays, the only change that might be made to the flowsheet would be to replace the wet separation process by some dry method, perhaps along the lines of the Doncaster Waste Treatment Plant, which produces air-classified lights for RDF production (section 2.5.1); alternatively, some sort of source separation scheme might be attempted, in which paper or newsprint was kept separate from the rest of household waste, for special collection and delivery to an acid hydrolysis plant.

Economic evaluations of process plants designed to hydrolyse cellulose by the new high temperature/short reaction time method have indicated that ethanol production from newsprint, sawdust and the cellulosic content of municipal refuse should be viable in a large enough plant able to handle slurries of high solids concentration (Porteous,1967,1975; Grethlein,1978; Emery and Kent,1979; Rugg and Brenner,1980). Unfortunately, most of the economic analyses that have been produced are not compararable, as they

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_1] This suggestion arose from a consideration of the kinetics of cellulose hydrolysis, a subject discussed in section 3.4.

differ on such factors as the size of the plant, the exact nature of the process, the starting material and its assumed price, the nature of the final product, the credit assumed for byproducts, and just how the authors have scaled up from laboratory data.

There is also a need to base projected costs on actual experimental work with sorted refuse. To date, cost analyses have been made using results from experiments with purified cellulose, wood, kraft paper or newsprint: but none of these necessarily reflects the real nature and properties of the raw material which is actually available. Refuse is an extremely unhomogeneous product, containing many impurities even when sorted (e.g. into air-classified lights), and any of these might influence the course of hydrolysis, either promoting or inhibiting the production of glucose from cellulose, or the subsequent fermentation to ethanol.

The proposed new method of acid hydrolysis has aroused much interest as a means of obtaining alcohol (or energy) from biomass. It has been suggested that it might be more profitable to investigate other cellulosic wastes, like agricultural residues, as possible feedstocks for an acid hydrolysis process. But Veal and Whalley (1981), in a recent article, have singled out domestic refuse as the most promising source of waste cellulose in Britain. It is produced all the year round, and has the advantage of an existing collection system. Crop wastes, being seasonal, would require high collection and storage costs. Other cellulosic wastes are not produced in sufficient quantities.

These conclusions bear out the findings of a report prepared for the Watt Committee on Energy (Emery and Kent,1979) which stated that of all the cellulosic wastes considered, sorted refuse was the only one which appeared to be energetically and economically feasible as an alternative source of raw material for alcohol production. This is on top of the fact that there is a need now to develop alternative methods of refuse disposal, for all the reasons described above.

The potential of acid hydrolysis as a refuse disposal method, and as a "renewable" source of energy or chemicals, may be appreciated from a very rough calculation of the amount of ethanol that might be produced in this

way. Assuming that only the refuse collected in the metropolitan areas would be treated (approximately 7 million tonnes); that the paper content of this refuse is 30%; that this paper contains 50% cellulose; and that the yield of ethanol from cellulose is 27% by weight (Goldstein, 1975) - a total of over 280 000 tonnes of ethanol would be produced. For comparison, the present annual production of ethanol in the U.K. is 250 000 tonnes (Veal and Whalley, 1981).

As for its effectiveness as a refuse disposal method, acid hydrolysis could be expected to remove between 20 and 40% of the weight of incoming refuse (depending on the paper content). Whether there would be any advantage in hydrolysing the vegetable and putrescible fraction as well would be the subject for another investigation (this material certainly contains some cellulose). If the metals, glass and plastics could be recovered too, as part of an integrated process, the overall reduction in the weight of incoming refuse could be as much as 60 to 80%.

Such a process would in effect amount to an extension of a Doncaster-type flowsheet, in which the material currently being produced as air-classified lights and sold as RDF pellets (at an unreasonably low price) would be hydrolysed instead and upgraded to ethanol, a much more readily accepted product and one that is easier to store, handle and transport, and which would fetch the going market price.

2.7 Summary

This chapter has examined the disposal of municipal solid waste in Britain, in terms of the quantities of waste arising, the composition of this waste, and the methods employed to dispose of it (chiefly landfilling and incineration). The increasing difficulty and cost of disposing of refuse - particularly in metropolitan areas - was noted. It was seen how greater volumes of waste are being produced, while existing landfill sites are being exhausted, and how the high cost of capital equipment is making incineration prohibitive as a viable alternative.

Five other methods of disposal were then explored, all of which aim to recover materials or energy from refuse. Mechanical sorting processes to

recover paper, glass, metals and other products from mixed refuse, were typified by the Doncaster Waste Treatment Plant, which was described in some detail. The production of RDF in place of paper recovery was also discussed. Pyrolysis and anaerobic digestion were reviewed very briefly to investigate the state of research in these fields.

Finally, the acid hydrolysis technique was described, which aims at converting the cellulosic content of refuse to glucose for fermentation to alcohol. The advantages offered by this process as an alternative method of refuse disposal were presented, in terms of the renewed interest in ethanol and "ethyl-chemicals"; the possibility of obtaining other chemicals besides from the hydrolysates, as well as lignin, which may be used as a process fuel; the more viable technology using high-temperature hydrolysis; the possibility of using air-classified lights as a feedstock, to produce a higher-grade product than RDF; and the fact that refuse has been singled out as the most promising source of waste cellulose in Britain for conversion to ethanol and other chemicals.

Current research into the acid hydrolysis of cellulose centres on the development of a continuous reactor in which the hydrolysis may be carried out efficiently, and with high yields of glucose, at the high temperatures and short reaction times proposed by Porteous (1967). In order to design and operate such a reactor, some knowledge is required of the physical and chemical characteristics of cellulosic materials, of the difficulties that may be encountered, and of the work that has been done previously in this field, especially in recent years. All this is the subject of the next chapter.

CHAPTER 3

ACID HYDROLYSIS OF CELLULOSE - CHEMICAL CONSIDERATIONS AND A REVIEW OF PREVIOUS WORK

3.1 Introduction

Efforts to develop commercial processes for the acid hydrolysis of cellulose in materials such as newspaper, refuse or other cellulosic wastes encounter two main practical difficulties. The first is related to the low chemical reactivity of cellulose compared to that of other polysaccharides such as starch. This means that high temperatures and pressures are required for the heterogeneous hydrolysis using dilute acids to proceed at any useful rate. The second problem is that these same conditions also favour the rapid decomposition of the sugars formed into various other (less desirable) products. The basic problem in developing an effective and economical commercial hydrolysis process, therefore, is as it has always been, to overcome the difficulty of hydrolysing the cellulose while minimising the decomposition of the glucose product.

The study of the hydrolysis of cellulose in wood, paper or refuse is further complicated by the presence of other compounds, such as hemicelulose and lignin, which are normally found associated with cellulose; and by the fact that cellulose itself contains two different fractions, crystalline and amorphous, which undergo hydrolysis at very different rates.

The present chapter begins with an examination of the chemical composition and molecular structure of cellulosic materials, and the reasons for the difficulty experienced in trying to hydrolyse the cellulose contained in these materials. Paper and refuse are then evaluated as possible cellulosic substrates for an acid hydrolysis process. A brief summary of the history of commercial dilute acid

hydrolysis processes is presented, followed by a detailed consideration of the mechanism and kinetics of cellulose hydrolysis, especially at high temperatures.

The remainder of the chapter is devoted to a review of recent research into the hydrolysis of cellulose at elevated temperatures, and the development of a continuous reactor for the treatment of cellulosic wastes. The results of numerous experiments carried out in small batch reactors are reported, together with details of recent successes in the design and construction of continuous reactors. The enzymatic hydrolysis of cellulose is discussed very briefly, and mention is also made of methods of pretreatment that have been developed to increase the susceptibility or "accessibility" of cellulose for reaction. The chapter concludes with a final discussion which summarises the achievements of previous research, and highlights the areas of research which still need to be explored.

3.2 The Nature of Cellulosic Materials

3.2.1 Chemical composition

Cellulose is the most abundant organic compound on earth. It is constantly being regenerated by the natural process of photosynthesis whereby plants, using energy derived from the sun, convert carbon dioxide and water to carbohydrates with the release of oxygen. In plants, cellulose is found as the principal component and chief structural material of the cell wall, giving plants their rigidity and form.

In chemical terms, cellulose is a polysaccharide, a long-chain molecule composed of repeating units of anhydrous glucose residues, joined together by beta-1,4-glucosidic bonds. The chemical formula for cellulose is $(C_6H_{10}O_5)_n$. Like other high-molecular compounds, cellulose is a polydisperse product, i.e. it consists of macromolecules of different degrees of polymerisation. The number of glucose units per molecule may range from 15 or less to as high as 10000 for naturally occuring ("native") cellulose. The molecular weight varies accordingly from less

than 3000 to over 1.5 million (Cowling,1975; Fan et al,1980).

As has been seen, the cellulose in municipal solid waste is found primarily in paper and paper products: these, in turn, are derived from wood. Any investigation of the hydrolysis of paper in refuse ought therefore to consider also the other components that make up the chemical composition of wood, viz. hemicellulose and lignin.

Hemicellulose is a generic name for another group of carbohydrates associated with the cell wall. These are also polysaccharides, but unlike cellulose, which is a homopolymer consisting solely of glucose residues, hemicellulose is composed mainly of heteropolymers, often branched, of various pentose and hexose sugars (xylose, mannose, glucose, galactose and arabinose being the most predominant) and some uronic acids. In general, the degree of polymerisation of hemicellulose is much less than that of cellulose, and is on average 100-200 (Nikitin,1966,chap 16).

Lignin, the third principal constituent of wood, is non-carbohydrate in nature. Instead, it is a random, complex three-dimensional polymer made up of aromatic compounds which are derivatives of phenylpropane. The chemical composition and precise structure of lignin have not yet been completely elucidated, owing in part to the fact that lignin is almost insoluble, and that its isolation from cellulose is effected only with difficulty and with changes to its molecular structure. Lignin removal on a technological scale is the basis of the chemical pulping industry (see section 3.2.3 below).

Cellulose, hemicellulose and lignin together constitute up to 90-95% of the weight of oven-dry wood. The proportions of these components varies according to the species of wood, the age of the tree, the ecological conditions of growth, and other factors; but, on average, wood may be said to contain 40-50% cellulose, 20-40% hemicellulose and 15-35% lignin. The remaining 5-10% is made up of waxes, fats, essential oils, tannins, soluble saccharides, and various other compounds (Nikitin, 1966, chap 21). Cellulose, hemicellulose and lignin also make up the chief constituents of other kinds of plant materials and their derivatives. Cotton is the purest naturally-occuring form of cellulose (>90%) whilst bast fibres

such as ramie, flax, jute and hemp all contain over 70% cellulose. The hemicellulose content of these materials is low: it is much higher in

Table 3.1

Composition of some cellulosic materials

	Approximate composition (% dry weight)		
	cellulose	hemicellulose	lignin
coniferous woods	40 - 50	20 - 30	25 - 35
deciduous woods	40 - 50	30 - 40	15 - 20
cotton[a]	94	2	-
ramie[b]	76.2	14.6	0.7
hemp[a]	74.4	17.9	3.7
bagasse[c]	43	35	14
wheat straw[d]	30	50	13
corn cobs[e]	30	48	14
sunflower husks[f]	30	33	28
wastepaper, mixed[g]	70-85	?	?
avicel[d]	100	-	-
MSW RDF[c]	61	22	9
newsprint[h]	60	20	15

a Encycl.Polym.Sci.Technol., 1965.
b Kirk-Othmer Encycl.Chem.Tech., 1979.
c Emert and Katzen, 1981.
d Lipinsky, 1979.
e Krull and Inglett, 1980.
f Nikitin, 1966.
g Dunlap, 1976.
h Higgins et al, 1981.

straws, grasses and reeds, and in agricultural residues such as corncobs, sunflower husks and sugarcane bagasse. These materials are also being investigated as possible substrates for acid hydrolysis. The typical composition of some cellulosic materials is shown in Table 3.1. As may be

seen, the lignin content of agricultural materials is usually lower than in wood, as it is in paper and paper pulp. Extensive processing is carried out in the manufacture of paper products, which considerably alters the chemical composition of wood, and its molecular structure. The subject of molecular structure is discussed in greater detail in the next section.

3.2.2 Molecular structure and chemical reactivity

The dominant physical characteristic of cellulose is its extreme insolubility. This may be put down to its molecular structure, which has been the subject of intense study over the last 30 to 40 years. A useful review of this work appears in Shafizadeh and McGinnis (1971).

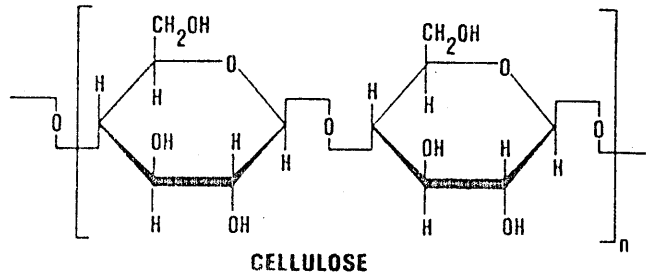
As a result of this work, it is now known that a high degree of crystallinity exists in the cellulose macromolecule, making it extremely resistant to chemical or biological attack. This is in marked contrast with starch, which is another polysaccharide composed only of glucose units, linked through the 1- and 4-positions; but in starch the glucose residues are bound by alpha-1,4-glucosidic bonds instead of beta (see Figure 3.1). This difference in stereochemistry results in two completely different molecular structures and in an enormous difference in physical properties, as may be seen from Table 3.2.

Table 3.2

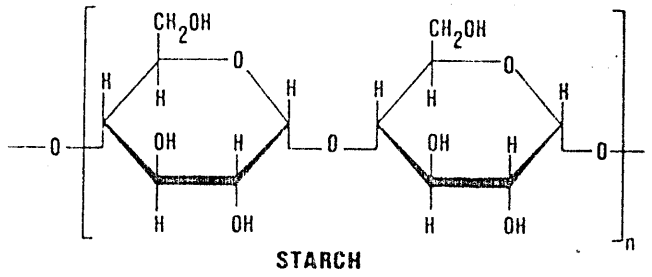
Physical properties of cellulose and starch

	cellulose	starch
chemistry	beta-1,4-glucan	alpha-1,4-glucan
chain structure	linear	branched
degree of polymerisation	>10 000	> 30 000
solubility	very poor	very good
degree of crystallinity	70-80%	40-50%
morphology	fibrous	granular

source: Marchessault and St-Pierre, 1980.



CELLULOSE



STARCH

Figure 3.1. Structural formulae of cellulose and starch (source: Huff, 1981).

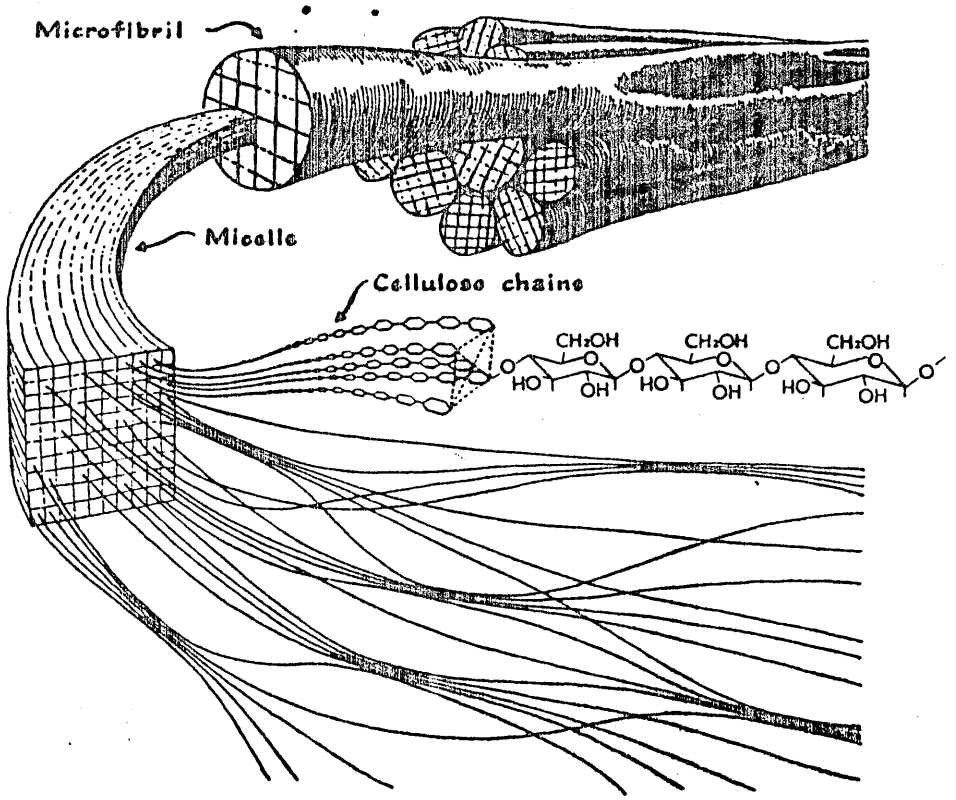


Figure 3.2. Cellulose microstructure (source: Moore and Barton, 1978).

Since the alpha-bond is axial, starch has an irregular or branched polymer framework, and an amorphous (noncrystalline) structure. But the beta-substituent is equatorial, so cellulose has linear chains with a regular repeating structure. In such cases, attractive forces between the chains favour an ordered array as opposed to completely random coils, and the solid polymer contains crystalline regions (Moore and Barton, 1978). This is borne out by X-ray diffraction studies on cellulose and extensive investigations with the electron microscope. These latter reveal that the cellulose in cell walls occurs as threadlike structures approximately 3.5 nm in width and of indefinite length. These are called elementary fibrils or protofibrils, and are the finest structural elements that have been observed. A number of these elementary fibrils aggregate into long slender bundles called microfibrils (see Figure 3.2) which in turn twine together in hollow cylinders called fibrils (Moore and Barton, 1978) These are visible under the optical microscope.

It is generally agreed that within the elementary fibrils the long-chain cellulose molecules are arranged neatly in a parallel alignment, and firmly bound together by numerous hydrogen bonds between hydroxyl groups of adjacent molecules (Fan et al, 1980). There is also a degree of hydrogen bonding within the linear molecule itself, as may be seen from Figure 3.3 (Zabriskie et al,1980). These inter- and intra-chain hydrogen bonds are very strong (each bond has a bond energy of 6000 to 12000 cal/mol, which compares with 50000 cal/mol for the beta-1,4-glucosidic carbon-oxygen bond (Zabriskie et al, 1980)) and impart rigidity to the cellulose polymer, preventing its solubility in water.

Other regions exist within the cell wall in which the cellulose chains are less ordered and may even be tangled - these are the paracrystalline or amorphous regions. Whether these disordered regions exist within the microfibril or in a layer of cellulose molecules surrounding it is still the subject of research and debate (Cowling, 1975); what is certain, however, is that the proportion of amorphous to crystalline material varies quite markedly from one cellulosic material to the next, although the ratio is generally quite small in the case of native cellulose.

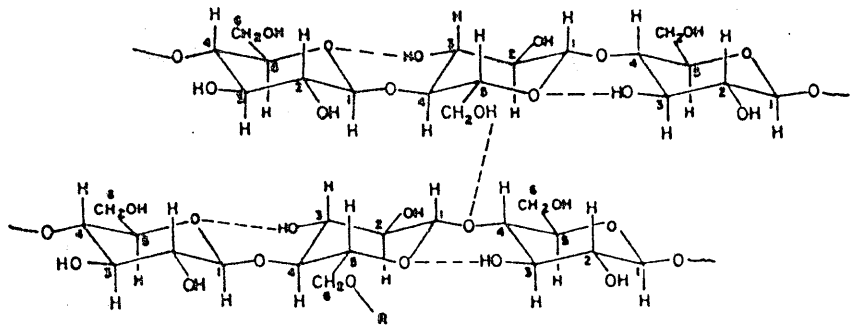


Figure 3.3. Intra- and inter-molecular hydrogen bonding in cellulose (source: Zabriskie et al, 1980).

These structural considerations are important from the standpoint of the acid hydrolysis reaction, as the rate of hydrolysis of crystalline cellulose is only a fraction of that of starch, and some form of physical or chemical pretreatment is required to modify the cellulose microstructure and increase the susceptibility of cellulose to reaction before hydrolysis by acids or enzymes will occur. Even then, it is usually found that high temperatures and pressures (in excess of 180°C and 1.24 MPa (180 psi)) are needed for dilute-acid hydrolysis to proceed at any appreciable rate.

This "inaccessibility" of cellulose for reaction is exacerbated by the presence of lignin, which grows into a large, random molecule completely surrounding or "encrusting" the cellulose microfibrils, rather like the cement poured over the reinforcing rods in prestressed concrete (Fratzke, 1974; Cowling,1975). The rate of hydrolysis, by large enzyme molecules in particular, is severely restricted (see section 3.6); hydrolysis by dilute acids is not so seriously affected, as the acid molecule is small, and can more easily penetrate the lignin. Lignin itself remains virtually insoluble during the hydrolysis, even hydrolysis by concentrated acids.

In complete contrast to cellulose and lignin, the third major component of cellulosic material, i.e. hemicellulose, is readily accessible to the action of dilute acids and alkalis. Hemicellulose is deposited within the cellulose microfibril, helping to cement the elementary fibrils together (see Figure 3.4): but the heteropolymerisation and high degree of

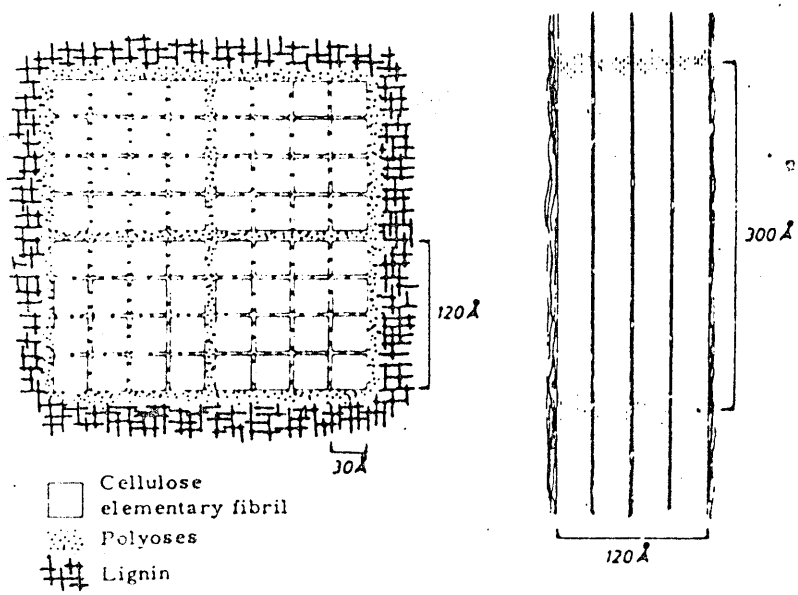


Figure 3.4. Ultrastructural organisation of the cellulosic components of wood (source: Fan et al, 1980).

branching of hemicellulose prevent it from forming regular, intermolecular hydrogen bonds or close, tight-fitting crystalline regions, and this increases its solubility. Hemicellulose hydrolysis with 0.1 to 1.0% aqueous sulphuric acid may be carried out at 95° to 120°C in short reaction times: the yield is primarily pentoses and hexoses (Hsu, Ladisch and Tsao, 1980).

During acid hydrolysis of cellulosic materials, then, the cellulose is hydrolysed with difficulty, the lignin for all practical purposes remains insoluble, while the hemicellulose is very rapidly hydrolysed to its constituent sugars, even at moderate temperatures. Physical or chemical pretreatment methods increase the susceptibility of cellulose for reaction, and its rate of hydrolysis may be speeded up by the action of strong acids at high temperatures and pressures.

3.2.3 Paper and refuse as cellulosic substrates

The largest single component of the cellulosic fraction of municipal solid waste is paper, which is derived from the cellulose contained in wood. Many different grades of paper are produced, and find their way into municipal refuse, ranging from high-grade writing paper to low-grade newsprint: each of these grades of paper varies in texture and cellulosic

content, and in the number and type of included additives, depending on its method of manufacture and the purpose it was designed to fulfill.

The production of paper from wood begins with one of a variety of mechanical or chemical pulping processes which are now available for reducing wood to the fibrous state. Mechanical pulping, as the name implies, involves separation of the wood fibres by purely mechanical means. Logs of wood are held against a grindstone, and the fibres are ground off in the presence of water. Except for a few water-soluble components, all the constituents of wood remain in the groundwood pulp. Yields of pulp from this process are therefore high - up to 95% - but the resulting paper has poor strength and cannot retain a bright appearance. This type of paper is used chiefly for the production of newsprint, which thus has substantially the same composition as wood (Updegraff,1971; Brown and Fitzpatrick,1976).

Chemical pulping processes employ chemical reagents to separate the cellulose fibres from the other wood components. The aim is to react the lignin to water-soluble salts, which may be easily removed from the pulp. Delignification is usually accompanied by various degrees of hemicellulose hydrolysis, and the overall yield of pulp is only about half the weight of the original wood: but the remaining cellulose is relatively pure and is used for the production of higher-grade papers.

Pulps can be used without bleaching (as in newsprint or brown wrapping and packaging paper) or they may be bleached with chlorine compounds to obtain the white fibres for printing, writing and tissue papers. A variety of additives also find their way into the formulation of different products: fillers, such as clays, give the opaque and smooth finish required for printing; waxes and resins impart strength and water resistance; and pigments and dyes are added for colouring (Brown and Fitzpatrick, 1976).

The paper fraction of municipal refuse typically contains many different kinds of paper and paper products, such as newsprint, printing paper (books and magazines), tissue paper, writing paper, paper bags, cartons, and corrugated cardboard boxes. A large portion is composed of

newsprint, which is by far the greatest end use of non-packaging paper (Quimby,1975). About 1.2 million tonnes of newprint are consumed annually in Britain: over 90% of the pulp is imported from Scandinavia, and is derived from the Norwegian or Sitka spruce (Wollen, 1982). The original wood contains about 43% cellulose, 28% hemicellulose and 29% lignin (on an extractives-free basis) with the hemicellulose being composed primarily of mannose and xylose residues (McGovern,1980).

The newsprint itself is made up of 70-75% groundwood, with the addition of 25-30% chemical pulp to give extra strength to the paper sheets. This increases the cellulose content of the resulting paper, and studies in the field of enzymatic hydrolysis have reported a value of 51% available cellulose in the "Guardian" newspaper (Halsted,1973). In the U.S.A., greater proportion of chemical pulp is added, and a much higher cellulose content results, e.g. 70% for the "Boston Globe" (Brandt et al,1972).

The paper in refuse is mixed in with all the other components, from which it must be separated if it is to undergo hydrolysis. A number of wet and dry separation processes have been developed to effect this separation; alternatively, some form of separation at source might be contemplated, especially for newspapers, as this is one material that the public has had some experience in collecting separately from the rest of household rubbish. A future refuse hydrolysis plant, therefore, might be fortunate to receive as its feed a dry, source-separated assortment of paper and paper products; otherwise, a sorting and classification process would be required, resulting in a feed to the plant not dissimilar to that presently produced at Doncaster and Byker for the manufacture of RDF (see sections 2.5.1 and 2.5.2). In order to accomodate both these options, the present work includes experimental work with newsprint (as a representative sample of source-separated paper) and air-classified lights from the RDF plant at Doncaster. Filter paper (pure cellulose) is used as a "control".

3.3 A Review of Early Commercial Acid Hydrolysis Processes

Attempts to develop commercially feasible processes for the acid hydrolysis of cellulose go back a long way, at least to the year 1900. It will be useful to review very briefly some of these early processes based on the use of dilute acids, as present-day research is in many ways a logical development of this early work.

Then, as now, the problem consisted in obtaining as high a yield of fermentable sugars as possible, by minimising the decomposition of glucose formed during the hydrolysis. To appreciate the kind of success achieved by these early workers, it should be remembered that wood has been the traditional raw material of the cellulose hydrolysis industry, and that wood contains, on average, about 45% cellulose based on the original dry wood weight.

The conversion of cellulose to ethanol may be described in chemical terms (with the numbers below referring to molecular weights) by the expression

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{hydrolysis}} nC_6H_{12}O_6 \xrightarrow{\text{fermentation}} 2nC_2H_5OH + 2nCO_2$$

cellulose	glucose	ethanol
162	180	92

Thus, 100 kg of dry wood should, on average, contain 45 kg of cellulose, which may be converted to 50 kg of glucose by hydrolysis, and then fermented to 25.6 kg of ethanol or 34 litres of 95% ethanol (for a ton of dry wood, the values would be 510 lb of alcohol or 82 U.S. gal of 95% ethanol) (Miller, 1975).

In the southern United States, between 1910 and 1922, there were two plants producing some 19 000 to 26 500 litres of 95% ethanol per day (5000 to 7000 U.S. gal) from southern yellow pine sawmill waste (Sherrard and Kressman,1945; Plow et al,1945). The process used was known as the "American" or one-stage process, which has also been called the Simonsen method (Nikitin, 1966, p561). This was a batch hydrolysis with 0.5%

sulphuric acid under steam pressure of about 912 kPa (about 9 atm). The conversion was accomplished in 15 minutes, but even in this short period of time, much of the sugar formed was decomposed. Other process losses reduced the yield further to an overall net 9.2 litres of 95% ethanol per 100 kg of wood (22 U.S. gal/ton). This yield was too low to be able to maintain competitive production when the local sawmills that supplied the plants were closed down, and raw materials had to be transported long distances from other areas at considerable cost. Simultaneously, the price of blackstrap molasses, the alternative source of industrial fermentation alcohol at that time, was lowered substantially, and these pioneering hydrolysis plants were forced out of operation.

But it was not too many years later that a German, Heinrich Scholler, developed a new technique that resulted in a very marked improvement in the yields of alcohol obtainable from the acid hydrolysis of wood. By allowing successive batches of hot dilute (0.8%) sulphuric acid to percolate through a stationary column of compressed wood waste at temperatures which increased from 120° to 180°C, and removing the sugars from the reaction zone immediately as they were formed, decomposition of glucose was reduced and yields of 21.7 to 24.2 litres of alcohol were obtained per 100 kg of oven-dry wood (52 to 58 U.S. gal/ton) (Locke et al,1945; Harris et al,1945). The pressure in the percolator began at 1.14 MPa and reached 1.24 MPa in the final batch (165 to 180 psi). The total extraction time was 13 to 20 hours. This method is known as "pulse percolation", and with some modifications, was used extensively in Germany before and during World War II. It was estimated that the combined capacity of Scholler plants in Germany by the end of the War was 10 million litres of alcohol per year (Locke et al, 1945).

In America, the Madison Wood Sugar Process, developed by the U.S. Forest Products Laboratory towards the end of World War II, was a refinement of the Scholler process, and represented an improvement in terms of alcohol yield. By allowing dilute acid to flow continuously through a charge of wood chips, with continuous removal of hydrolysate, decomposition problems were reduced even further, as the sugars were in contact with the acid for an even shorter time. Using 0.5 to 0.6% sulphuric acid at 150° to 180°C, yields of 26.9 litres of 95% alcohol were obtained per 100 kg of dry, bark-

free Douglas fir wood waste (64.5 U.S. gal/ton) in under three hours of hydrolysis time (Harris and Beglinger,1946).

A full-scale sachharification plant based on the Madison Process was designed and built at Springfield, Oregon, with an estimated capacity of 15 million litres of ethanol per year. But unfortunately, the plant was never operated commercially. The end of the War, and with it the shortage of alcohol, combined with the advent of cheap naphtha and synthetic ethanol from ethylene derived from oil and natural gas led to the premature shutdown of the Oregon plant, and the abandonment of work on the acid hydrolysis of cellulose for over 20 years in the Western hemisphere.

As far as is known, only in the controlled economy of the U.S.S.R. has acid hydrolysis of cellulosic materials established itself firmly at the industrial level. The first Soviet hydrolysis plant was built in Leningrad in 1935 (Karlivan,1980), and at present there are thought to be over 40 plants in existence, with a combined annual output of some 400 000 tons of wood sugar (Humphrey,1979). The process used is one of periodic percolation (Pohjola,1977), in which liquid flows continuously through a stationary bed of solid, as in the Madison Process. Modifications have been made in the design of the percolator vessel, to improve the hydrodynamic flow conditions, assuring both a horizontal and vertical flow of liquid through the percolator; but the basic process remains the same (Karlivan,1980). A great deal of fundamental research has been conducted in the Soviet Union during the last three decades aimed at developing improved methods of hydrolysing wood and agricultural wastes. But because the published results are in Russian, and are often not readily available, this work has been largely ignored outside that country.

3.4 The Mechanism and Kinetics of Cellulose Hydrolysis

It has been said that, "Hydrolysis among chemical reactions is like water among solvents - the most frequently encountered and the least understood" (Moelwyn-Hughes,1971). And certainly, the hydrolysis of cellulose and cellulosic materials is no exception, but has engaged and

stimulated the attention of numerous investigators for well over a hundred years.

Chemically, the hydrolysis of cellulose by dilute acids is similar to that of the simpler and more easily studied disaccharides. It involves the formation of an intermediate complex between the glucosidic oxygen atom (connecting the glucose residues) and a proton, followed by the splitting of the acetal bond adjacent to $C_{(1)}$ with the addition of water. The mechanism of the reaction is shown in Figure 3.5.

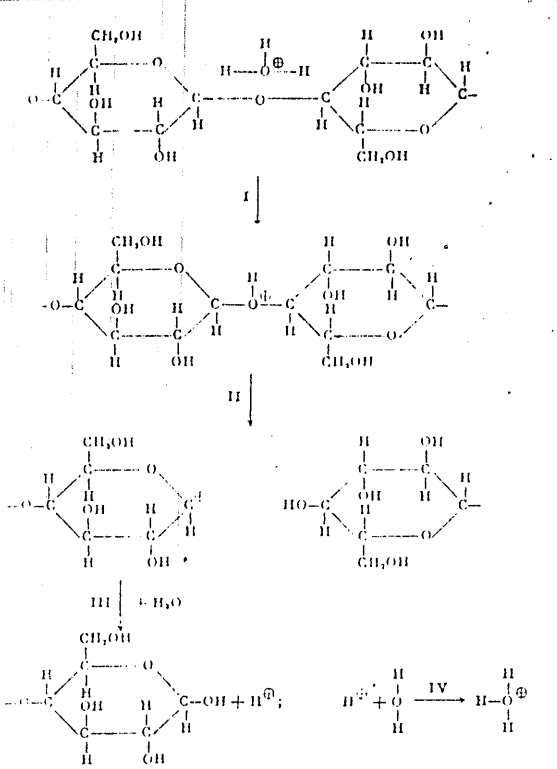


Figure 3.5. Mechanism of cellulose hydrolysis (source: Nikitin, 1966).

The hydrolysis does not proceed immediately to the monosaccharide stage, but is gradual, with the formation of intermediate products of shorter chain length (Nikitin,1966,p556). The various steps in the process may be represented schematically as follows (adapted from Wenzl, 1970, chap4):

$$\text{native cellulose} \xrightarrow{\text{I}} \text{stable cellulose (hydrocellulose)} \xrightarrow{\text{II}} \text{soluble oligosaccharides} \xrightarrow{\text{III}} \text{glucose}$$

. . . . . equation 3.1

In contrast to the hydrolyses of similar but noncrystalline carbohydrates, which proceed rapidly to completion, the hydrolysis of cellulose by the action of dilute acids is extremely slow at moderate temperatures. This is not true of all the parts of the cellulose, however: it was observed many years ago that the rate of cellulose hydrolysis, as measured by the weight loss associated with the formation of soluble oligosaccharides (Davidson,1943) or by the continuous estimation of the glucose produced (Nickerson,1941a,1941b) is initially rapid, and only subsequently very much slower. It was deduced from this that the readily degraded fraction could be equated to the more accessible amorphous content - thereby providing an experimental means of determining the latter (Nickerson and Habrle,1947).

The difference between the rates of hydrolysis of amorphous and crystalline cellulose may be appreciated from Figure 3.6, which shows the weight loss for a natural and a regenerated cellulose on hydrolysis with strong hydrochloric acid at the boil for a number of hours (Nelson,1960). The logarithm of the residual weight is plotted as a function of time. The initial rapid rate of weight loss, corresponding to the hydrolysis of the amorphous regions, is represented by the curved portions of the graphs, while the rate curves representing the hydrolysis of the crystalline regions are linear.

It has in fact been found that the rate of weight loss during the later stage of hydrolysis is accurately semilogarithmic for all cellulosic materials. Figure 3.7 shows more data, for a range of natural and regenerated celluloses (Millett, Moore and Saeman,1954). Such linear relationships are indicative of a reaction following first-order kinetics: the rate constant may be determined from the slope of the line, and from similar lines plotted at different temperatures for the same material the Arrhenius activation energy for the equation may be calculated. Extrapolation to zero time gives an estimate of the initial crystalline

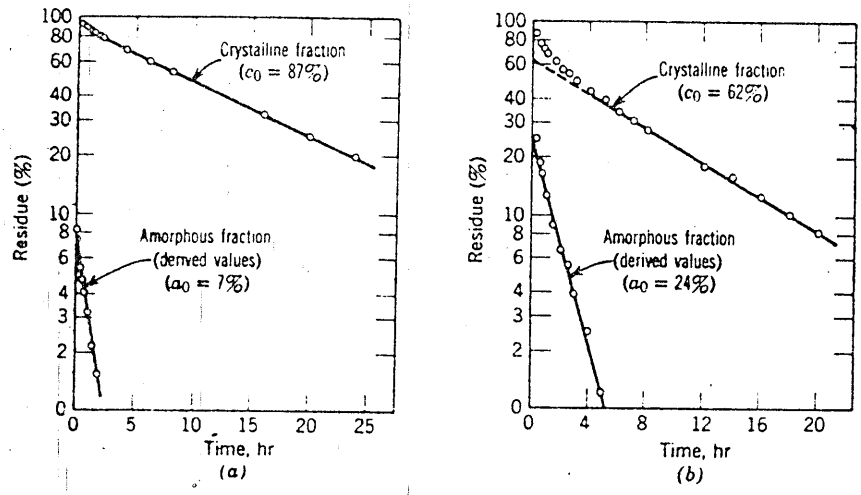


Figure 3.6. Weight-loss curves of cellulosic materials hydrolysed with hydrochloric acid: (a) cotton linters, 100°C, 6N`HCl; (b) viscose rayon, 100°C, 4N`HCl (source: Nelson, 1960).

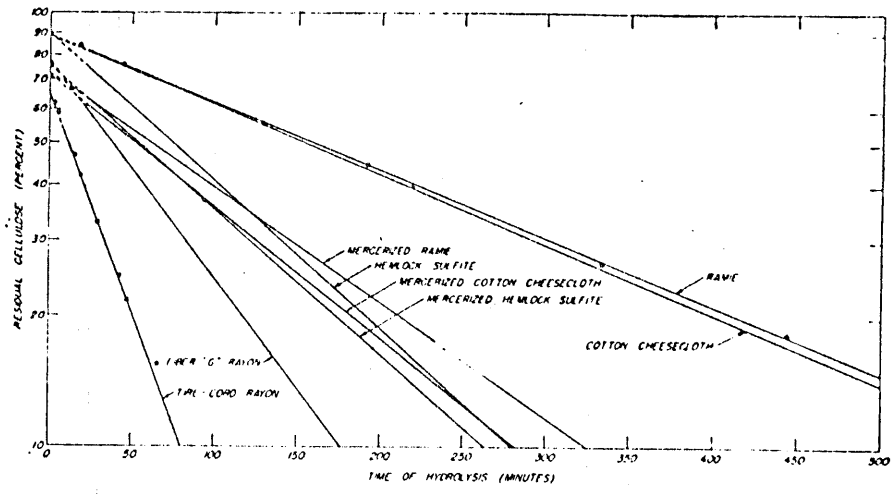


Figure 3.7. Weight-loss curves for several cellulosic materials on acid hydrolysis (Millett et al, 1954).

cellulose content of the sample, while the difference between the extrapolated values and the measured values of percentage residue at times represented by the curved portions of the line gives an estimate of the percentage of the amorphous fraction remaining at these times. These derived values are plotted as the lower curves in Figure 3.6; as may be seen, first-order reaction kinetics are once again indicated, while the difference between the rates of hydrolysis is quite substantial.

Several explanations have been put forward for this semilogarithmic relationship. It appears that in the reaction sequence set out in equation 3.1, steps (I) and (III) are rapid, even under mild hydrolytic conditions, while step (II) is slow and is the rate-determining step. This step corresponds to the degradation of "stable cellulose" or "hydrocellulose" to soluble polysaccharides. Investigation has shown that hydrocellulose takes the form of rod-shaped particles or crystallites, whose length depends on the nature of the original cellulose and on the conditions of hydrolysis. Sharples (1957,1958) concluded that the crystallite lengths in hydrocellulose are exponentially distributed, and that acid attack is on the ends of these particles. He attributed the variation in the rate of hydrolysis from one cellulosic material to the next (see for example Figure 3.7) to the different number of particle ends present in each system. Battista (1950) studied hydrolysis under mild and drastic conditions, and deduced that the more drastic the conditions of hydrolysis, the shorter the crystallite lengths would be, and hence the more rapid the progress of the reaction.

All these investigations were conducted not so much to study the acid hydrolysis reaction, but rather with a view to determining cellulose fine structure. In the experiments, strong acids were used at generally moderate temperatures and hydrolysis times measured in hours, days or even weeks (Battista,1950). Commercial cellulose hydrolysis, on the other hand, which has as its objective the production of glucose for fermentation, uses acid concentrations below three percent at temperatures above 150°C to accelerate the rate of hydrolysis and thereby reduce the reaction time significantly. It is known, however, that the same reaction conditions result in the decomposition of glucose, and this is a crucial factor that has to be taken into account when studying the acid hydrolysis of

cellulose at high temperature. The first person to report a detailed study of the factors affecting the kinetics of cellulose hydrolysis and glucose decomposition in dilute acid at high temperatures was Jerome Saeman (1945).

Working at the U.S. Forest Products Laboratory during World War II, Saeman (1945) conducted his investigation as part of the work that went into the development of the Madison Process for wood saccharification, already mentioned above in section 3.3. He studied (separately) the kinetics of cellulose hydrolysis and glucose decomposition at 170°, 180° and 190°C with catalyst concentrations of 0.4, 0.8 and 1.6% sulphuric acid. Samples of glucose dissolved in dilute sulphuric acid were placed in sealed glass bombs and heated to the desired reaction temperature for various times in a rotating autoclave, and then cooled rapidly and analysed for residual sugar. Similarly, samples of Douglas fir ground into fine particles of 0.5 mm or less (<30 mesh) were hydrolysed with sulphuric acid in sealed bombs for various times, using a liquid-solid ratio of 10 to 1.

Saeman employed a novel way of analysing the residue of the hydrolysis samples. After a sample had been heated for a predetermined time, it was cooled, filtered and washed. The filtrate was made up to a fixed volume and analysed for sugar using the conventional Shaffer and Somogyi method (1923), while the the residual cellulosic material was subjected to a quantitative saccharification, using a method developed at the Forest Products Laboratory itself (Saeman, Bubl and Harris,1945), followed by sugar analysis. The amount of unhydrolysed carbohydrate in the residue was then expressed as grams of sugar potentially available per 100 grams of starting material. This made the calculations simpler and relied on a method of analysis which at the time and for its purpose could be considered superior to any available cellulose analysis.

On plotting the results from his hydrolysis experiments, Saeman found the same semilogarithmic relationship as described above for residual cellulose content vs. the time of hydrolysis. Saeman was actually one of the first to observe this phenomenon, and to describe the hydrolysis of cellulose as a pseudo-first-order reaction. The plot of his results for

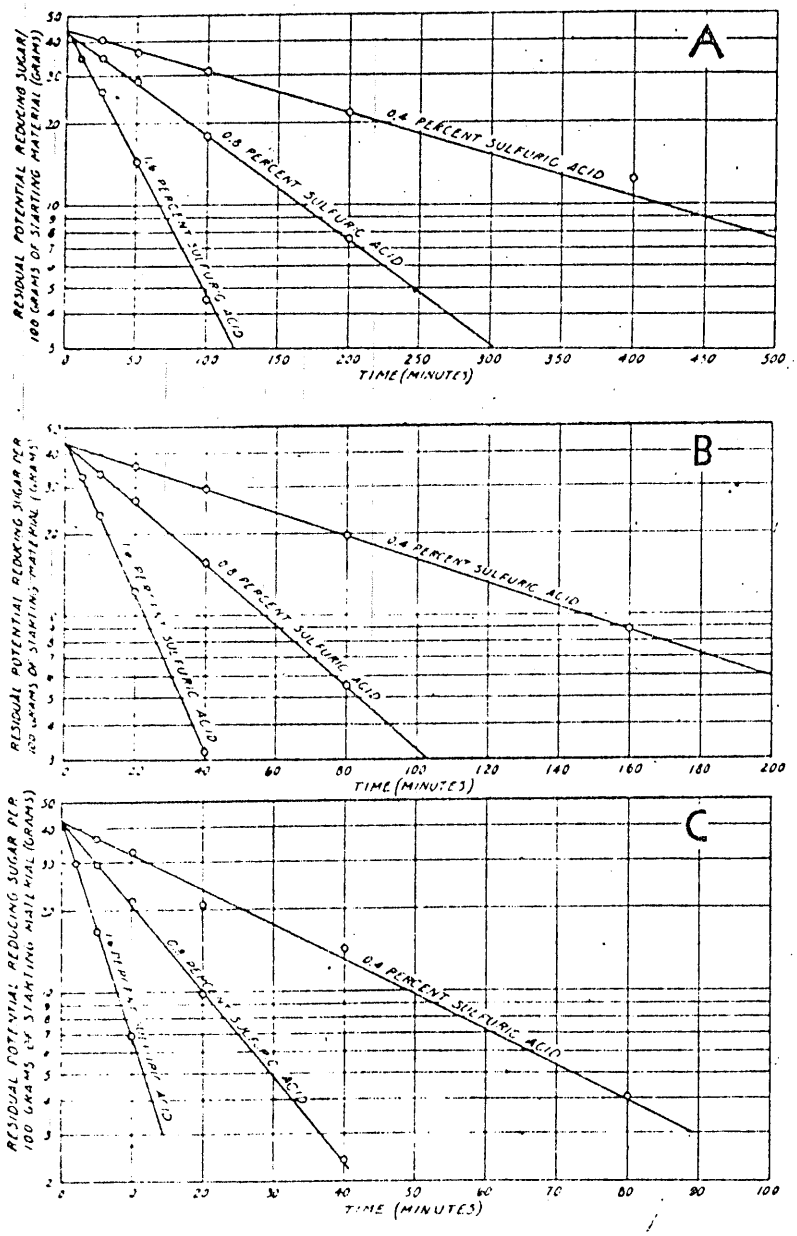


Figure 3.8. Hydrolysis of Douglas fir at 170°C (A), 180°C (B) and 190°C (C) (source: Saeman, 1945).

three different acid concentrations at three different temperatures is reproduced in Figure 3.8.

Saeman also noticed that the relationship applied only to the resistant or crystalline portion of the cellulose. From a quantitative saccharification of his original starting material, he found that it contained 66.6% potential reducing sugar; while the amount of resistant cellulose in the sample, estimated by extrapolation of the rate curves to zero time, was 44%. The difference between these values he took to

represent an easily hydrolysed fraction of the wood which had already reacted by the time the samples reached the temperatures of hydrolysis.

From the slopes of the lines in Figure 3.8, Saeman calculated the values of the first-order reaction rate constants k_1 for the hydrolysis of Douglas fir cellulose, and with the knowledge of these values he was able to derive a value of the Arrhenius activation energy, E_1. Finally, he determined the dependence of the rate of hydrolysis on the acid concentration. He combined all these effects into a single expression which simultaneously described the dependence of the rate of hydrolysis on the temperature and acid concentration. The expression had the general form:

$$k_1 = P_1 . C_a^m . e^{-E_1/RT} \qquad \text{. . . . . equation 3.2}$$

where P_1 = a constant, empirically derived, 1.73×10^{19} min^{-1}

C_a = the acid concentration, in weight percent

m = a constant, empirically derived, 1.34

E_1 = the activation energy, empirically derived, 42 900 cal/mol

R = the universal gas constant, 1.9872 cal/molKelvin

T = the absolute temperature, Kelvin

In his investigations of the decomposition of glucose, Saeman used exactly the same graphical techniques and procedures to plot his results, and discovered that this reaction too followed a first-order rate law, and that the expression relating the reaction rate constant k_2 to the temperature and acid concentration was identical in form to equation 3.3 above, i.e.

$$k_2 = P_2 . C_a^n . e^{-E_2/RT} \quad \text{..... equation 3.3}$$

where P_2 = a constant, empirically derived, 2.39×10^{14} min^{-1}

C_a = the acid concentration, in weight percent

n = a constant, empirically derived, 1.02

E_2 = the activation energy, empirically derived, 32 870 cal/mol

R = the universal gas constant, 1.9872 cal/molKelvin

T = the absolute temperature, Kelvin

Since the hydrolysis of cellulose and the decomposition of glucose could both be written as first-order reactions, Saeman concluded that the overall reaction scheme could be described by a kinetic model of two first-order consecutive reactions:

$$\text{cellulose} \xrightarrow{k_1} \text{glucose} \xrightarrow{k_2} \text{decomposition products}$$

..... equation 3.4

This is a commonly discussed reaction scheme, the differential equations for which are as follows (Frost and Pearson, 1961, p166):

$$dC_A/dt = -k_1 C_A \quad \text{..... equation 3.5}$$

$$dC_B/dt = k_1 C_A - k_2 C_B \quad \text{..... equation 3.6}$$

$$dC_C/dt = k_2 C_B \quad \text{..... equation 3.7}$$

where in this case C_A refers to the concentration of cellulose at time t, C_B is the concentration of glucose, and C_C the concentration of the decomposition products. Integration of equations 3.5 and 3.6 gives the following formulas for the concentrations of cellulose and glucose in the reaction:

$$C_A = C_{AO}e^{-k_1 t} \qquad \text{. . . . . equation 3.8}$$

$$C_B = C_{AO}\frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \qquad \text{. . . . . equation 3.9}$$

C_{AO} is the initial cellulose concentration and the integration assumes that neither glucose nor any decomposition products are present at the start of the reaction. If they are, the integration becomes more complicated, and another term appears in equation 3.9.

Examining these reactions more closely reveals that the concentration of cellulose C_A decreases constantly with time t, the concentration of decomposition products C_C increases constantly, while the concentration of glucose C_B rises to a maximum and then falls away (see Figure 3.9). By further calculation it may be shown that the maximum value of C_B is a function of the ratio of the rate constants, k_1/k_2 (Frost and Pearson,1961,p168). The higher the value of k_1/k_2,the greater will be the value of C_B at its maximum. This is really as one would expect from a simple examination of equation 3.4; the more rapid the rate of formation of glucose relative to its rate of decomposition, the greater should be the maximum yield of glucose during the hydrolysis. The value of the maximum yield and the reaction time needed to produce this yield, are given by the equations:

$$C_{B_{max}} = C_{AO}(K)^{1/(1-K)} \qquad \text{. . . . . equation 3.10}$$

$$t_{max} = \{1/(k_1 - k_2)\}\ln(K) \qquad \text{. . . . . equation 3.11}$$

where $K = (k_1/k_2)$ is the selectivity. All these equations, strictly speaking, apply only to homogeneous reactions. The value of Saeman's work is that it shows that they may nevertheless be used with very adequate results to describe the heterogeneous hydrolysis of the resistant or crystalline portion of cellulose.

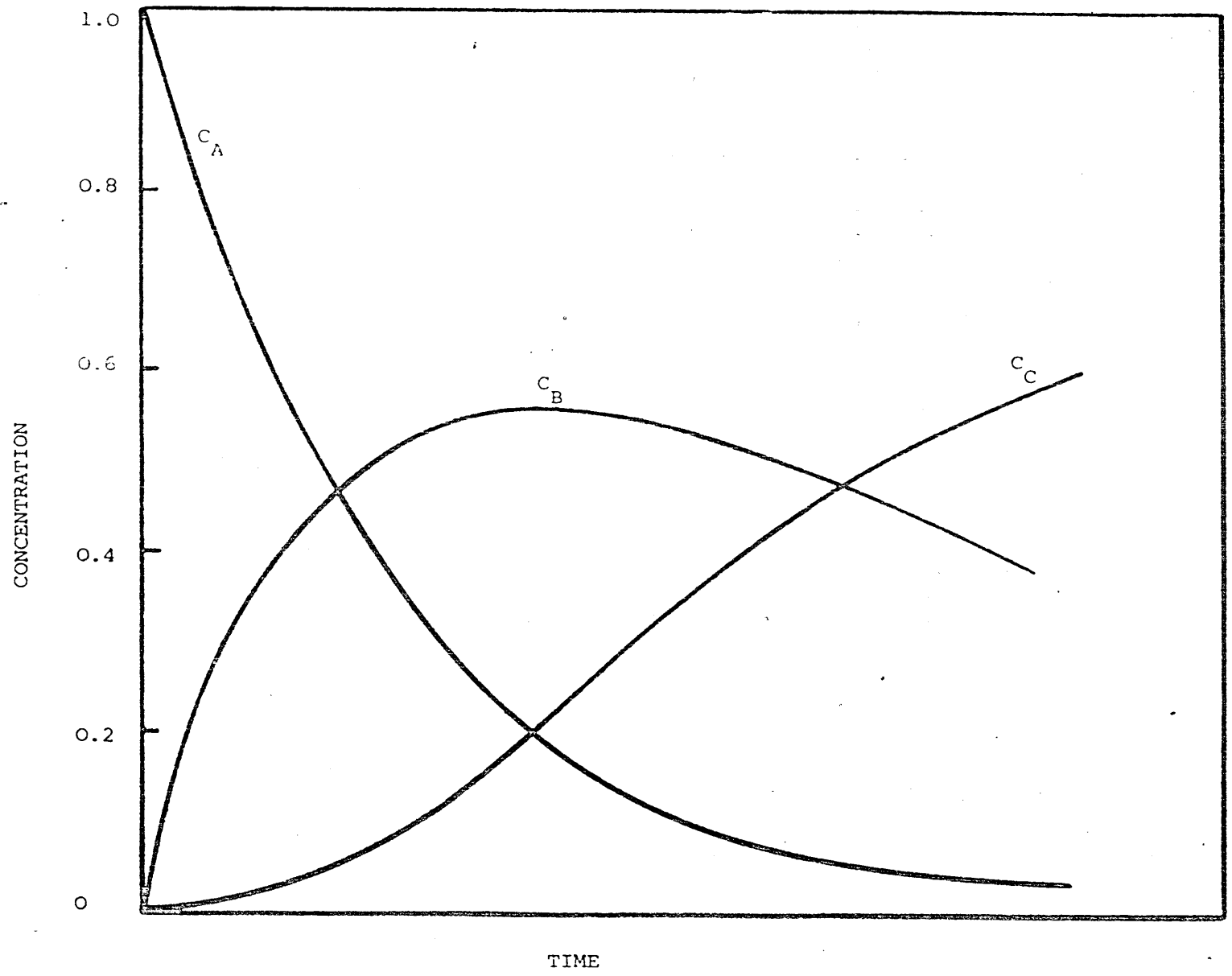


Figure 3.9. Concentration-time curves for substances A, B and C in consecutive first-order reactions.

Saeman verified his analysis by predicting the course of a hydrolysis reaction from the values of k_1 and k_2 determined under isothermal conditions. Using equation 3.9, he derived an expression for predicted glucose yield as a function of the time of hydrolysis. He was then able to compare observed and calculated values at various times of hydrolysis. In each case, he found the values to be in close agreement.

Looking back on Saeman's work with the benefit of hindsight, it may be seen as a logical extension of the work of other cellulose chemists to higher temperatures. Generally, these experimenters have not used such drastic conditions of hydrolysis as Saeman did, but even at lower temperatures, on calculating the rate constants and activation energies for the hydrolysis of crystalline cellulose, they have found that the rate constant k_1 increases with increasing temperature and/or acid concentration (Philipp et al,1947). Battista (1950) made this point explicitly in his comparison of mild and drastic conditions of hydrolysis. Saeman found this too, in his experiments, and more. He observed that the ratio k_1/k_2 increased with increasing temperature and/or acid concentration, resulting in greater predicted maximum yields of glucose, which he detected in his experiments. Higher yields of glucose were obtained from the hydrolysis of Douglas fir cellulose when the reaction was raised from 170° to 190°, and the sulphuric acid concentration from 0.4 to 1.6 percent (Figure 3.10).

This point was taken up more than 20 years later when Porteous (1967), then a graduate student at Thayer, was working on a one-month design project. His objective was to find a profitable way of disposing of refuse, and he hit upon the idea of an acid hydrolysis of the cellulosic material to glucose, followed by fermentation to ethanol. He began by assuming that the kinetic data collected by Saeman for the hydrolysis of cellulose in wood would apply equally well to the cellulosic material in refuse - a seemingly reasonable assumption, as paper and paper products make up the greatest proportion of the cellulosic content of refuse, and paper is derived primarily from wood. Newsprint in particular, which is made (mostly) from wood subjected to a purely mechanical pulping process, has essentially the same composition as wood.

With the aid of the Arrhenius rate equation, Porteous calculated the values of the rate constants k_1 and k_2 for temperatures up to 230°C, using Saeman's values for k_1 and k_2 at 170° and 0.4 percent acid as reference. Substituting the values he found into equations 3.8 and 3.9, he predicted that a maximum yield of 55.2% sugar should be obtainable after only 1.285 min of reaction time if the temperature of hydrolysis was 230°C. Table 3.3 shows the results of his kinetic computations, clearly indicating how the predicted maximum sugar yield increases with temperature, and the corresponding dramatic decrease in optimum reaction time.

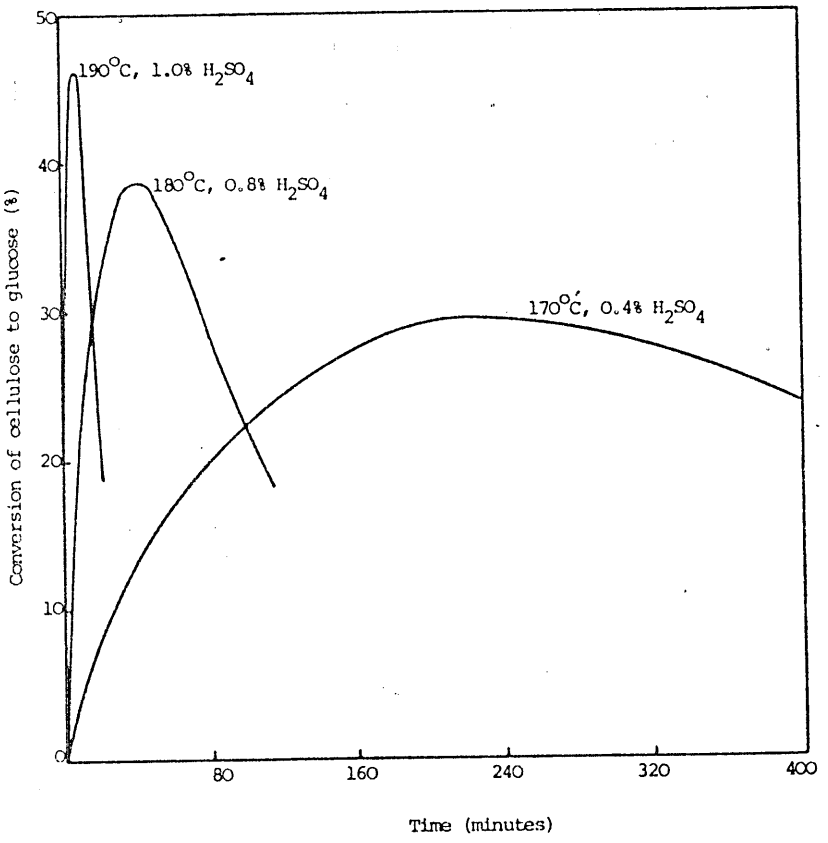


Figure 3.10. Predicted glucose yields for isothermal hydrolysis of Douglas fir cellulose (after Saeman, 1945).

Table 3.3

Kinetic computations for 0.4% acid at 170° to 230°C

temp °C	k_1	k_2	k_1/k_2	$C_B$max %	t_{opt} (min)
170	0.00355	0.00534	0.66479	29.58	228
190	0.02936	0.02685	1.0932	38.43	35.599
210	0.20385	0.11816	1.7251	47.14	6.36
230	1.21320	0.46209	2.6254	55.22	1.285

source: Porteous, 1967.

Because the reaction time was so much smaller than that required in the traditional wood hydrolysis processes, Porteous was able to recommend that the hydrolysis be carried out in a continuous reactor instead of the conventional batch percolators. A plug-flow reactor was suggested in preference to a continuous stirred tank reactor, as it allows a greater yield of intermediate product to be obtained from first-order consecutive reactions, where k_1 is greater than k_2. The economic implications of this were quite dramatic, as a plug-flow reactor in which the reaction was carried out very swiftly would be roughly 200 times smaller than the equivalent batch or semi-batch reactor handling the same throughput. As a result, capital outlay would be reduced considerably, and because the process was being applied to refuse disposal, extra savings would be made because of reduced disposal costs. An economic evaluation of a plant designed around this idea suggested that ethanol production from the cellulosic content of refuse should be profitable - especially when treating U.S. refuse with its high (60%) paper content (Porteous, 1967).

Porteous' predictions were based on two assumptions: that the kinetic parameters derived by Saeman from his experiments with Douglas fir cellulose could be used to calculate the rate of hydrolysis of the

cellulose in paper, and that the kinetic values determined at 170° to 190°C could be accurately extrapolated to higher temperatures using the Arrhenius rate equation. Both of these assumptions needed to be tested in practice, as did the suggestion that the reaction be carried out in a continuous plug-flow reactor. Recent research into the acid hydrolysis of cellulose has been concerned with these issues.

3.5 Review of recent research

3.5.1 Batch reactors

The longest programme of work aimed at verifying the predictions of Porteous and developing a continuous reactor for cellulose hydrolysis has been under way at the Thayer School of Engineering, Dartmouth College since the late 1960s. The initial experiments were by Fagan (1969) who carried out batch tests similar to those of Saeman but at much higher temperatures, and showed that the kinetic model of two consecutive first-order reactions could be applied equally well to describe the hydrolysis of cellulose in paper.

He hydrolysed small (0.5 g) samples of kraft paper, ground to a particle size less than 2 mm, and mixed with 20 ml of acid solution, in glass culture tubes placed inside a sealed 1"x4" stainless steel nipple. This vessel, containing the sample for hydrolysis, was placed in a constant temperature oil bath, previously heated to 260°C. The temperature-time history of each sample was recorded, temperature being measured by a thermocouple inserted into a special thermowell which screwed onto the cap of the nipple. At various values of the reaction temperature up to 240°C, samples were removed from the bath, quenched in ice water, and analysed for glucose content. Experiments were carried out using 0.2, 0.5 and 1.5% sulphuric acid, and the highest glucose yield obtained was just over 30%.

The data obtained from these non-isothermal batch reactions were analysed by assuming that Saeman's kinetic model of first-order consecutive reactions was valid, and using a non-linear regression programme to determine the rate constant parameters P_1, P_2, m, n, E_1, and E_2

which provided the best fit of the experimental data to the computed values of sugar yield as a function of time and temperature. Values of the rate constant parameters so determined are listed in Table 3.4. With these values, Fagan drew up a similar set of curves for the hydrolysis of paper as Saeman had obtained for the hydrolysis of wood. This graph is reproduced in Figure 3.11 (Fagan et al, 1971). It was calculated, furthermore, that under isothermal reaction conditions, a maximum conversion of cellulose to glucose of 52% would be obtained at 230°C using 1% sulphuric acid.

This figure was different from Porteous's prediction of 55.2% maximum yield using 0.4% sulphuric acid at the same temperature. This was because the values of the kinetic parameters were not the same as (though they were similar to) those of Saeman, which are also listed in Table 3.4 for comparison. But the principle had been proven, that high yields of glucose may be obtained from the hydrolysis of cellulose in very short reaction times, if the temperature is raised to 220°C or over. The results also confirmed Saeman's findings that the reaction rate constants k_1 and k_2 increased as temperature and acid concentration increased, with k_1 increasing faster than k_2. Fagan also hydrolysed two samples of ground refuse by the same experimental method, and found that it was possible to predict the glucose yields using the kinetic data developed from kraft paper (Grethlein,1975).

Other researchers have since carried out similar tests using a variety of cellulosic substrates, and have obtained kinetic data from their results. Using an almost identical procedure to that of Fagan, Guha et al (1978) at the University of Auckland in New Zealand investigated the hydrolysis of Pinus radiata sawdust, and found rate constants in close agreement with those determined by Saeman for Douglas fir wood - the parameters are listed in Table 3.4. Experiments were conducted using 1% sulphuric acid and a liquid to solid ratio of 30:1, at temperatures of 180°, 190°, and 220°C. The highest glucose yields obtained were just below 30%.

At the Westinghouse Research Laboratories in Pittsburgh, PA, Vaux and Santini (1975) conducted batch hydrolysis studies with samples of

Table 3.4

Kinetic parameters for cellulose hydrolysis as determined by various researchers

substrate	experimental conditions	P_1 (min^{-1}) $\times 10^{19}$	m	E_1 (cal/mol)	P_2 (min^{-1}) $\times 10^{14}$	n	E_2 (cal/mol)	references
Douglas fir	170° - 190°C isothermal batch	1.73	1.34	42 900	2.38	1.02	32 870	Saeman, 1945
Kraft paper	180° - 230°C nonisothermal batch	28	1.78	45 100	4.9	0.55	32 800	Fagan et al, 1971
Solka-Floc	180° - 240°C isothermal plug-flow	1.22	1.16	42 500	3.79	0.69	32 700	Thompson and Grethlein, 1979
Paper pulp	not reported	0.615	1.275	48 660	1.42	0.997	37 540	Alpay, 1974
Pinus radiata sawdust	190° - 220°C nonisothermal batch	1.95	1.45	41 440	2.15	0.9	32 470	Guha et al, 1978
Lignocellulose residue	205° - 228°C nonisothermal batch	2.79	-	44 500	1430	-	39 900	Pohjola et al, 1977a
Oak sawdust and other cellulosic materials	204° - 216°C isothermal plug-flow	0.44	1.00	42 900	0.028	1.80	30 000	Church and Wooldridge, 1981
Oak sawdust and other cellulosic materials	204° - 216°C isothermal plug-flow	1.73	1.34	44 000	2.38	1.02	33 400	Church and Wooldridge, 1981

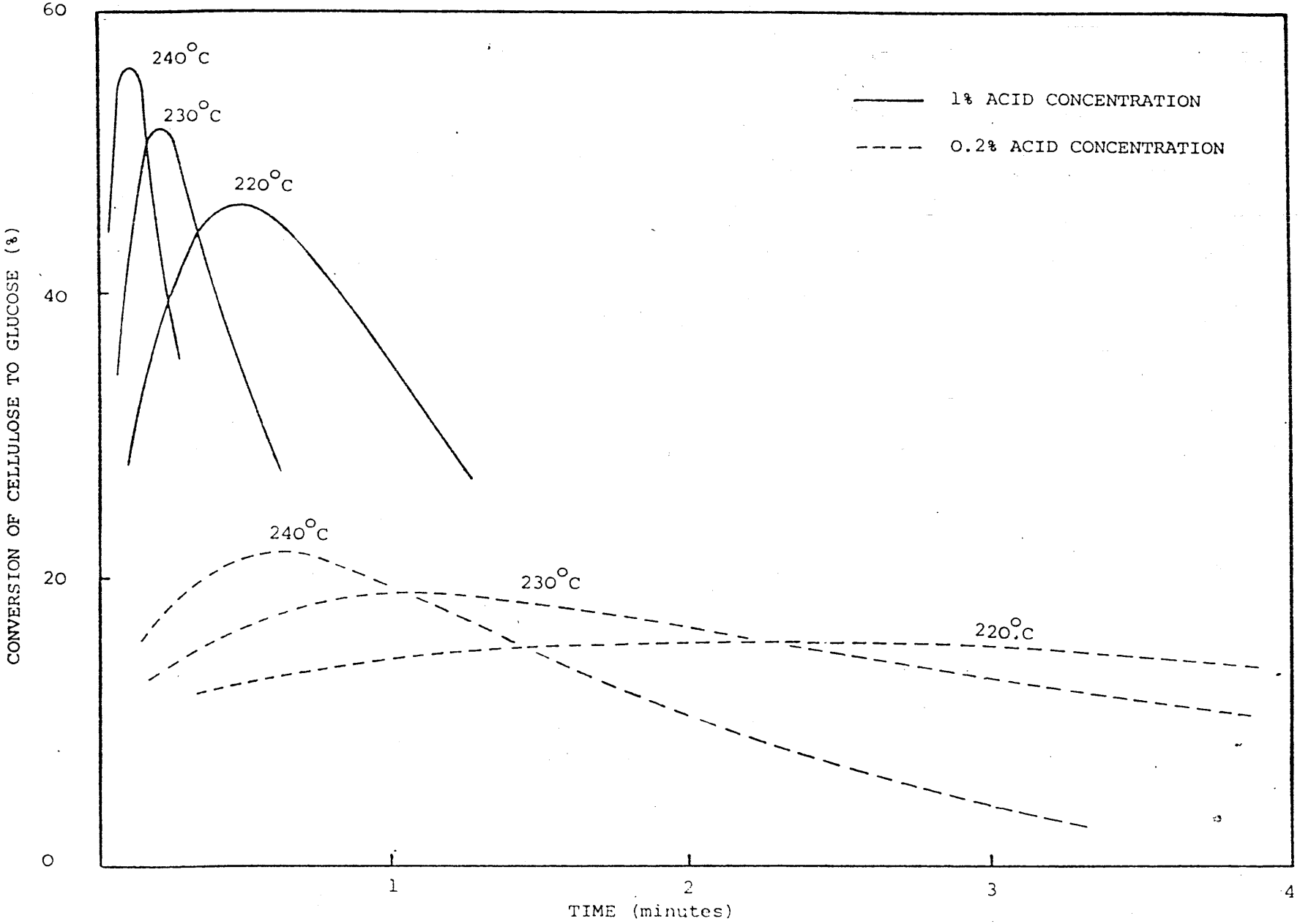


Figure 3.11. Predicted glucose yields for isothermal hydrolysis of paper (after Fagan et al, 1971).

shredded newspaper, using a similar experimental method. They carried out their tests with 1% sulphuric acid, and a liquid to solid ratio of 10:1, at temperatures of up to 230°C. They compared their experimentally observed glucose concentrations with yields predicted using Fagan's kinetic parameters, and found the results to be in close agreement.

A different experimental method was employed by Pohjola et al (1977a) at the Technical Research Centre of Finland. They carried out the hydrolysis of a lignocellulose residue in a 2-litre stirred pressure reactor in which the slurry was preheated to the desired reaction temperature, and acid injected under nitrogen pressure. Reaction time was counted from the moment the acid was fed (instantaneous mixing of acid in the slurry was assumed). Samples were removed from the reactor through a condenser by opening a valve. Experiments were thus carried out under isothermal conditions, at temperatures of 205° to 228°C. The sulphuric acid concentration was 0.5%, and the liquid to solid ratio 30:1. Yields of glucose of almost 50% were obtained. The kinetic parameters derived are also listed in Table 3.4.

Alpay (1974) also carried out experiments into the hydrolysis of cellulose using a stirred pressure reactor, although the work was limited to a maximum temperature of 180°C. The substrate studied was waste paper pulp, and reactions were carried out with 0.4, 0.8 and 1.6% sulphuric acid and a liquid to solid ratio of 10:1. The work was done at Imperial College of Science and Technology, London. The kinetic parameters derived are also listed in Table 3.4.

Finally, Rugg and Brenner (1980) of New York University's Department of Applied Science carried out the hydrolysis of used newspapers in 1-litre and 5-litre stirred autoclave reactors. Details of these batch experiments are not reported, although the optimum reaction conditions found were said to be temperatures of around 220° to 230°C, and reaction times of less than 30 seconds with about 1% sulphuric acid. Yields of glucose of up to 50% or more of the available cellulose were said to have been obtained. Kinetic parameters were not determined.

3.5.2 Continuous reactors

The experimental work carried out under batch conditions confirmed the predictions of Porteous (1967) that high yields of glucose could be obtained from the hydrolysis of cellulose by dilute acids at temperatures of 220°C or more, in very short reaction times. The kinetic parameters obtained from the hydrolysis of cellulose in paper were not identical with those of Saeman (1945) but were sufficiently close to encourage work to proceed with the development of a continuous reactor. The advantages to be gained from carrying out the hydrolysis of cellulose in a plug-flow reactor at high temperature and short residence times have been discussed above (section 2.6) - but the problems involved are nonetheless considerable, and relate to the extreme reaction conditions of temperature and pressure required to hydrolyse the cellulose, the necessity of removing the glucose product swiftly from the reaction zone once it is formed (in order to minimise glucose decomposition) and the need to use materials that will be resistant to the highly corrosive conditions of strong mineral acid at high temperatures. Physical problems of solids handling and carrying out a controlled heterogeneous reaction at high solid-liquid ratios only add to the complications, especially when the residence time of material in the reactor is so short.

The capabilities required from a continuous process include, among other things: continuously conveying a high-solids cellulosic slurry to the reactor; increasing the temperature and pressure in the reactor to the optimal hydrolysis conditions; adding the required amount of acid catalyst; effecting the reaction in the optimum reaction time to obtain maximum glucose yield; quenching the products of the reaction swiftly to minimise glucose decomposition; and recovering the glucose continuously and efficiently from the hydrolysate. The development of a flow reactor along these lines has for several years been the subject of investigation by a number of groups of researchers, in different parts of the world.

Once again, the longest programme of work has been conducted at the Thayer School of Engineering, where Porteous first conceived the idea of applying high-temperature cellulose hydrolysis to refuse disposal. After Fagan's (1969) initial programme of batch experiments, a flow reactor was

designed and constructed to examine the acid hydrolysis of cellulose in refuse: this work is described in Converse et al (1973). Slurries of up to 1% ground refuse were pumped through a heater and mixed with concentrated sulphuric acid before entering the reactor, which was a 1.5 m (5 ft) long tube made of 1/4" Carpenter-20 steel. At the end of the reactor was a micrometering valve which was operated manually to control the pressure in the reactor. Slurry coming out of this valve entered a condenser, to be cooled to 25° to 30°C before being collected.

Many problems were experienced when operating this reactor. Acid and slurry flow rates were difficult to set at prior levels and keep steady, and momentary clogging of solids in the needle valve caused fluctuations in the reaction temperature. The reactor never actually ran for long without it plugging up (Grethlein, 1981). Although isothermal operation was assumed, reaction temperature was found to drop by 4° to 6°C along the reactor length during the experiments: this would have caused errors in calculating the predicted glucose yields, especially at high temperatures. Temperature was measured at the tube wall, at five points along the reactor length. The observed values of glucose yield were mostly around 20%, although one result of 53.5% was obtained, at 226°C using 1.07% acid at a residence time of 0.269 minutes. It was found that the yields could be quite well predicted using the kinetic parameters of Fagan et al (1971) developed from the batch experiments with kraft paper.

Work at Thayer continued, and a number of years later a reactor was developed in which the hydrolysis of cellulose could be carried out under controlled conditions. The design and evaluation of this reactor has been described by Thompson and Grethlein (1979). In their work, slurries of up to 13.5% Solka-Floc of particle size finer than 74 microns (-200 mesh), or 5% newsprint of particle size finer than 0.2mm (-65 mesh) were pumped at about 300 ml/min through a heating unit of 6 kW capacity which consisted of 26 m of concentrically coiled tubing wrapped with electrical heating tapes. The slurry temperature was raised from 30° to 240°C, while the fluid velocity was maintained at a sufficiently high level to prevent the slurry particles from settling.

A controlled flow of concentrated sulphuric acid was injected into the preheated slurry in a specially designed mixing tee, shaped like a venturi, with the final concentration of acid being between 0 and 2.0%. The acidified slurry then entered the reactor, made of Carpenter 20 cb3 stainless steel, and mounted vertically to prevent the settling of slurry particles. The reactor was in fact a series of tubes of various lengths which could be interchanged to vary the residence time.

On leaving the reactor, hydrolysate passed through a 1.8 m long capillary tube of 0.7 mm i.d. This was found necessary to maintain a pressure differential of 3.45 to 4.14 MPa (500 to 600psi) across the reactor. The hydrolysate was cooled as it passed through the capillary by means of a cooling water jacket, which lowered the temperature from 240° to 50°C in only a fraction of a second.

The results of the experimental work showed that 50 to 55% conversion of cellulose to glucose could be obtained repeatedly from the Solka-Floc slurries when operating in the temperature range 235° to 240°C at a residence time of 0.22 min with 1.0% sulphuric acid. These and other results obtained from the same substrate at 0.5, 1.5 and 2.0% sulphuric acid concentration, at temperatures varying from 180° to over 240°C, were used to estimate the kinetic parameters P_1, P_2, m, n, E_1, and E_2 in equations 3.2 and 3.3 above. This set of parameter values is also listed in Table 3.4, together with the values determined by other researchers for various cellulosic substrates under different reaction conditions.

Thompson and Grethlein (1979) also found that the parameter values derived for the acid hydrolysis of Solka-Floc could be used equally well to predict glucose yields from the hydrolysis of the cellulose in newsprint, despite the fact that the newsprint was the result of a different manufacturing process, had a higher hemicellulose and lignin content than Solka-Floc (see Table 3.5), and was ball-milled and sieved at a different size. On the basis of a previous preliminary process design (Grethlein,1978), they believed their results to be of commercial interest for slurries of solids concentrations greater than 10%.

Table 3.5

Composition of cellulosic materials used in previous continuous hydrolysis tests

composition of substrate (dry basis)	Solka-Floc	newsprint
glucan	88.2%	48.6%
mannan	2.1%	7.2%
xylan	7.9%	9.7%
lignin	0.5%	32.0%

source: Thompson and Grethlein, 1979.

Although the work at Thayer was begun with the aim of developing a process for refuse hydrolysis, no work has been reported in which the new reactor has been used to treat a refuse feedstock. Instead, the use of dilute acid hydrolysis as a pretreatment to enzymatic hydrolysis has been studied (Knappert et al,1980), and the emphasis seems to have shifted to the evaluation of agricultural residues and short-rotation forestry crops (poplar, pine, corn stover and bagasse) as substrates for cellulose hydrolysis (Grethlein,1981).

Another group of researchers which has constructed and operated a continuous reactor for cellulose hydrolysis at elevated temperatures is in the New York University Department of Applied Science. Working in association with Werner and Pfleiderer, manufacturers of extruder equipment, Rugg and Brenner (1980) developed a twin-screw hydrolysis reactor which was used to treat sawdust and paper pulp at about 240°C and 3.45 MPa (500 psi) at low residence times (10 to 20 seconds).

Normally, a machine of this type would be used in the plastics industry to melt, mix and squeeze polymers through a die to form products of various sizes, shapes and colours. In its application as a hydrolysis reactor, however, sawdust or pulped newspapers were fed into the machine instead, and carried forward through the barrel by the twin co-rotating screws. The shearing action of the screws performed a pretreatment function by breaking up the cellulose, making it more accessible to reaction. At the same time, excess water was pressed out and removed, leaving a very dense cellulosic slurry which formed a plug in the screws and thereby prevented the backflow of material as the pressure built up toward the front of the barrel. All the time, heat was applied to the slurry in the barrel indirectly by superheated steam. When the desired conditions of pressure and temperature were reached, at a point shortly before the reactor exit, dilute sulphuric acid was injected into the system. The residence time of slurry in the reactor was measured from that point onwards. The reaction products were discharged from the end of the barrel through a high-pressure valve (Anon, "Continuous cellulose to glucose process", 1979).

Although no details of experiments carried out with this extruder reactor have been reported, it has been claimed that up to 90 kg/hr of

sawdust (containing 95% solids) or paper pulp (10% solids) may be treated continuously, with conversion of cellulose to glucose reaching 50 to 55% with 1 to 1.5% sulphuric acid (Anon, "New process converts cellulose waste into high Btu alcohol fuel", 1980; Remirez, 1981).

One of the particular advantages of this extruder reactor was that it had a modular design with interchangeable scews and barrel sections, which could be altered to suit the specific conditions required at different points along the reactor length, e.g. high shear action, increased pressure generation. In addition, as the acid was introduced so late into the process, just before the reactor exit, only the forward sections of the barrel needed to be made from corrosion-resistant materials.

The development of this extruder reactor is an important step towards the establishment of an industrial continuous hydrolysis process. Of particular significance are the high throughputs and the capacity of the reactor to treat slurries with high solid-liquid ratios. It is believed that a $28 million industrial plant based on this process is being built at Vicksburg, MS, to convert waste from cotton gins and sawmills into alcohol fuels (Reuse recycle, 1981). The plant will have an initial capacity of 4 million gallons of alcohol per year. Unfortunately, this group has published none of its experimental results with the continuous reactor, although work is said to be under way to optimize the reaction conditions for optimum glucose yield (Rugg and Brenner,1980). The estimation of kinetic parameters has not been mentioned either - but in a reactor of this type, it is probably very difficult to model the flow regime accurately, and scaling up would be done empirically with the aid of the in-house expertise of the extruder manufacturer.

A continuous hydrolysis reactor operated at much lower temperatures has been described by Pohjola (1977) at the Technical Research Centre of Finland. This system, incorporating a screw pump for feeding slurry continuously into the reactor, was designed for the hydrolysis of various cellulosic materials which are difficult to hydrolyse by percolation methods because of their poor permeability. A preheater was designed in such a way that the temperature of the reaction mixture could be raised by either external or direct steam heating, with heat transfer being assisted

by means of an internal rotating shaft fitted with scrapers. Product from the reactor was discharged into a flashing chamber by a periodically operating ball valve.

A typical substrate, chosen to test the performance of the apparatus, and to check the reproducibility of kinetic data obtained from batch tests was slightly decomposed moss peat, which contained a high proportion of cellulose in the amorphous form. The peat was ground in a Wiley mill to a particle size of 1 mm or less, and made into a slurry with dilute sulphuric acid. The final liquid to solid ratio was 8 or 9 to 1, and the acid concentration 0.5%.

Results are reported in which the reaction temperature was maintained at 169° to 173°C, and the residence time varied between 10 and 20 min. Glucose yields were steady at 39 to 40% of theoretical, and compared very favourably with results obtained from hydrolysis in a batch reactor. The flow reactor was said to operate very steadily throughout the experiments. This work has been the basis of a pilot hydrolysis plant (the Tampella/Pohjola process) which has been in operation in Finland for a number of years, investigating the production of ethanol from biomass (Hamala and Pohjola, 1980).

Another continuous hydrolysis system which has been operated at temperatures lower than those proposed by Porteous (1967), but higher than those used in conventional percolation hydrolysis, is that of Church and Wooldridge (1981). Their reactor was designed and constructed from sections of flanged 1.5" (40.9 mm i.d.) jacketed Schedule 40 Carpenter 20Cb-3 steel pipe, of a total length of 9.1 m. Instrumentation flanges were inserted between pipe sections, drilled and tapped for thermowells and pressure transducers. At the beginning of the reactor was an injection block, through which high-pressure steam and sulphuric acid were introduced to bring the slurry up to reaction conditions nearly instantaneously.

A novel feature of this system was the pump - this was a high-solids twin-ram pump designed by the experimenters, capable of feeding damp lignocellulose of particle size 1 to 2 mm at up to 40% dry solids. The

pump delivered slugs of material to the acid and steam injection block at the reactor inlet through a specially designed ball valve. The reactor was preheated by circulating oil through the jackets at the desired temperature, after which the system was pressurised with steam to 1.4 MPa (200 psi). The acid and biomass pumps were then started, and adjusted to their proper rates. (The nominal input capacity of the reactor was one dry metric tonne per day).

After a while, pressure built up to the usual operating level of 1.72 MPa (250 psi), at which point the process valve at the end of the reactor was set to maintain this pressure automatically. Rising pressure caused the stem of the valve to rise slightly, relieving increments of hydrolysed slurry through a jacketed cooling section to be collected. This pressure control system also controlled the temperature in the reactor:this did not vary more than 1^{o} to $2^{o}C$ over its entire length.

Results of experiments carried out with this reactor are reported for oak sawdust, newspaper, wheat straw, sugar cane bagasse, potato pieces, and whole grain corn (Church and Wooldridge, 1981). Newspaper hydrolysis carried out at $204^{o}C$, 3.3 min residence time, and with 18% initial reactor solids after acid and steam injection gave glucose yields of about 35% (based on potential glucose) when the acid concentration was between 2 and 2.5% in the aqueous phase. Results obtained in an earlier part of the work, when a Moyno pump was being used to pump an 8% slurry of <8 mm newspaper at 5.5% solids gave yields of up to 40% at $216^{o}C$ and 2 min residence time, using 1.4% acid in the aqueous phase. Lower yields were obtained at $202^{o}C$ even after 4 or 6 min residence time.

As neither the kinetic parameters derived by Saeman (1945) nor those of Thompson and Grethlein (1979) fitted the experimental data, a search was made for a new set of parameter values: the values found to fit the glucose yield data for the hydrolysis of oak sawdust were found to fit the rest of the data acceptably well too. These values are listed in Table 3.4. It was also found that by modifying the Saeman parameters by changing the values of E_1 and E_2, a set of values was produced which could be used to predict most of the data reasonably well.

Finally, at the Open University in Milton Keynes, a programme has been under way since 1976 to develop a continuous reactor for the hydrolysis of cellulose in refuse. Porteous and Anderson (1980) designed and constructed a rig which was used to carry out experiments with knife-milled filter paper and computer paper, and to produce hydrolysate for fermentation studies. On account of problems with blockages, however, and inadequate temperature control, glucose yields were low and not very consistent, and kinetic data was impossible to obtain. One run (240°C, 2% acid and 5.88 min residence time) produced a conversion of cellulose to glucose of 30%, but generally glucose yields were less than 5%. A description of this reactor is given in Chapter 4, together with details of how it was modified to enable it to be used to carry out the continuous hydrolysis of cellulosic feedstocks under controlled conditions.

3.6 Enzymatic Hydrolysis

Parallel with the research which has been going on in the last 10 to 15 years to develop a reactor for the continuous dilute acid hydrolysis of cellulosic materials, has been another programme of work aimed at achieving the same objective (ethanol from cellulosic wastes) by enzymatic action. This work is based on the use of cellulose enzymes derived from mutant strains of the fungus Trichoderma reesei (formerly T. viride) which can be produced by growing the fungus in a culture medium containing cellulose and nutrients. The fungus is then filtered out, and the enzymes are recovered in solution, available for reaction. Cellulosic material is mixed with the enzyme broth in a reactor at 50°C and at pH adjusted to 4.8; the reaction produces glucose, which may be recovered by filtration (Vesilind and Rimer, 1981, chap6).

The advantages of enzymatic hydrolysis over acid hydrolysis are that acid corrosion resistant equipment is not required, as the harsh conditions of temperature and acid concentration do not apply; and that higher yields of glucose can be expected, as no decomposition takes place at the low temperatures employed, and as the enzymes are specific in their action, no byproducts are formed. The disadvantages are that intense physical or chemical pretreatment is required to make the cellulose

susceptible to enzymatic attack, and that the residence times for high conversion of cellulose to glucose are long, necessitating the use of large (and hence more costly) reactors.

Because the enzyme molecule is large, the crystallinity of cellulose and the association of cellulose with lignin pose a much greater barrier to enzymatic hydrolysis than to acid hydrolysis, where the acid molecule is small and can easily penetrate the lignin (Fratzke et al, 1974). The pioneering work in the field of enzymatic hydrolysis has been carried out by researchers at the U.S. Army Natick Development Centre in Massachusetts, who have established that extensive ball milling is easily the most effective pretreatment for reducing cellulose's crystallinity - but this is a very expensive operation, and makes the economics of the whole process unfavourable at present (Slesser and Lewis, 1979, chap4).

It should be said, however, in favour of classified municipal solid waste with its high paper content, that unlike native cellulose found in whole plant forms, it is a source of cellulose which has already undergone a considerable amount of physical and chemical degradation (during pulping) which promotes the susceptibility of cellulose for hydrolysis (Horton et al, 1980). But this is not to say that additional processing is not required to enhance the rate of enzymatic hydrolysis of cellulose in refuse - the same authors go on to discuss various kinds of chemical, microbial and mechanical pretreatments, concluding that some form of thermomechanical pretreatment would be preferred from the technical and economic point of view (ibid.). The subject of pretreatment methods for cellulose hydrolysis is discussed in more detail in section 3.7, below.

The other serious limitation of enzymatic hydrolysis is the long residence time required to produce glucose by this method. Table 3.6 shows the results of Millett et al (1979) who investigated the effect of vibratory ball milling on the hydrolysis of various cellulosic materials. As may be seen, for the hydrolysis of newsprint, 2 to 4 days were required to achieve the high yields of glucose that are obtainable by enzymatic hydrolysis. There are indications that recent improvements in technology would allow the hydrolysis time of shredded, slurried refuse (separated from the inorganic constituents) to be reduced to about 24 hours (Wise et

Table 3.6

Effect of vibratory ball milling
on enzymatic hydrolysis of newsprint

time of milling (min)	% saccharification					
	1 day	2 days	4 days	8 days	10 days	16 days
0	--	41.1	53.3	53.9	--	55.6
10	--	58.2	67.2	68.1	--	69.5
30	61.1	73.6	75.4	--	79.2	--
60	70.4	79.6	83.0	--	85.3	--
120	81.5	87.5	89.8	--	91.8	--

source: Millett et al, 1979.

al, 1981a), but this is still very long compared to the 20 or 30 seconds required for hydrolysis by dilute acids at high temperature.

Other advances that have been made in the technology of enzymatic hydrolysis in the last 10 years have been in improving the yield and concentration of enzyme produced in fermentation broths, and in developing improved mutants and optimising fermentation conditions. But the production of ethanol by enzymatic hydrolysis and fermentation is still estimated to be almost twice as costly per tonne of municipal solid waste treated, compared with producing ethanol by the acid hydrolysis route (Wise and Kispert, 1981). An earlier comparison of the acid and enzymatic hydrolysis of newsprint showed that the cost of making glucose by enzymatic hydrolysis was more than twice as much, when the slurry concentration to the acid hydrolysis reactor was 10% (Grethlein, 1978).

3.7 Methods of Pretreatment

The methods of pretreatment just described with respect to enzymatic hydrolysis may also be used to accelerate the hydrolysis of cellulose by dilute acids. The pronounced difference between the rates of hydrolysis of crystalline and amorphous cellulose has already been noted (section 3.4; and see Figure 3.6). Substantially reducing the crystallinity of cellulose, thereby making it more readily available for reaction, would allow acid hydrolysis to be carried out effectively at much lower temperatures than presently required for useful reaction rates: this would mean that decomposition of glucose would cease to be such a major problem. Alternatively, during hydrolysis at elevated temperatures, if the accessibilty of cellulose for reaction were increased, the ratio of the rate constants k_1/k_2 would be higher, and greater maximum yields of glucose would be obtainable.

Perhaps the most dramatic method of pretreatment yet suggested is that employed in the Tsao-Purdue process, which relies on the use of chemical solvents to completely destroy the crystallinity of cellulose by extracting it from a cellulosic residue, and then reprecipitating it in an amorphous form which is much easier to hydrolyse under less stringent

reaction conditions (Ladisch et al, 1978; Hsu et al, 1980). The solvents suggested are Cadoxen (a mixture of cadmium oxide and ethylenediamine), ferric tartrate or concentrated sulphuric acid. This reaction scheme is in fact the basis of a quantitative saccharification technique (Saeman, Bubl and Harris, 1945), but it is the first time that this established knowledge has been suggested for use in a commercial process. A serious drawback of this scheme, however, is the prohibitive cost of solvent recovery, and there are no reports of this process ever having been tested outside the laboratory.

A review of the more usual methods of cellulose pretreatment was made several years ago by Millett et al (1975). The chemical methods considered were swelling with alkaline agents, such as sodium hydroxide or ammonia; delignification or the use of delignified residues as raw materials; and steaming. Physical pretreatments reviewed included fine grinding; irradiation by gamma-rays or high-velocity electrons; thermal treatment at high or low temperatures; and compression. All of these methods proved effective to varying degrees (depending on the substrate used and the conditions of hydrolysis) in improving cellulose hydrolysis.

With specific reference to the recent work which has been carried out to develop a continuous reactor for cellulose hydrolysis by dilute acids, Thompson and Grethlein (1979) used Solka-Floc particles which had been ground and sieved to a particle size finer than 74 microns, or newsprint of particle size finer than 0.2 mm; Brenner et al (1977) preferred hydropulping followed by low-level electron irradiation (5 to 10 Mrad) in their batch experiments with used newspapers; and Pohjola et al (1977a) investigated the hydrolysis of a lignocellulose residue, which had been blown out of a reactor after steam digestion, with the fibrous structure of the particles partly destroyed. This latter investigation led to the development of the Tampella/Pohjola process (Hamala and Pohjola, 1980), and is reminiscent of the Iotech process of "steam explosion" which has been described by Marchessault and St.Pierre (1980); this process is said to produce 98+% pure cellulose and 95+% pure lignin through solvent extraction of the lignin (Huibers and Jones, 1980). The cellulose retains its crystallinity, however, and has been used as a substrate for enzymatic hydrolysis.

Finally, integrated acid/enzyme hydrolysis systems are under investigation, in which acid hydrolysis is used as a pretreatment stage to make the substrate more susceptible to enzyme hydrolysis. The work at Thayer has recently gone in this direction. The same continuous plug-flow reactor that was designed and constructed by Thompson and Grethlein (1979) (see section 3.5.2 above) was used to carry out a partial hydrolysis of Solka-Floc,newsprint, corn stover and oak chips as a pretreatment to enzymatic hydrolysis. Slurries containing 5% solids were hydrolysed for 0.22 min at temperatures ranging from 160° to 220°C and acid concentrations of 0.4 to 1.2%. These pretreated substrates were then subjected to enzymatic hydrolysis at 50°C for up to 48 hr. The work has been described by Knappert et al (1980).

The results showed that the native substrates in particular (the oak and the corn stover) gave much improved yields of glucose after pretreatment compared with enzymatic hydrolysis without pretreatment. On the other hand, newsprint, which gives a much higher yield of glucose on enzymatic hydrolysis than does oak (when neither of them are pretreated) was not so much improved after pretreatment, except if the temperature of the acid hydrolysis was about 220°C, when quantitative yields of glucose would be obtained after 24 hr of enzymatic hydrolysis. Applying the results of these investigations to the light fraction of municipal refuse, a cost analysis showed that single-pass dilute acid hydrolysis was in fact still 20 to 25% cheaper in terms of ethanol production cost than enzymatic hydrolysis with dilute acid pretreatment (Converse and Grethlein, 1979).

3.8 Summary and Conclusions

In this chapter, the nature of cellulosic materials has been investigated, from the point of view of hydrolysing the cellulose contained therein to glucose. It has been seen that in Nature, cellulose occurs in close association with two other macromolecules, hemicellulose and lignin, the former of which is more readily hydrolysed than cellulose, while the latter is essentially inert. It has also been seen that cellulose occurs in both crystalline and amorphous forms, which are hydrolysed at very different rates.

Studies of the kinetics of cellulose hydrolysis have shown that the hydrolysis to glucose and the subsequent decomposition of glucose at the same reaction conditions, may be quite adequately described by the kinetic model of two first-order reactions in series. The original work of Saeman (1945) was extended to higher temeperatures by Porteous (1967), who predicted that high yields of glucose would be obtained from cellulose hydrolysis at very short reaction times, under these conditions. This has since been shown to be the case, from experiments carried out in both batch and continuous reactors.

The original purpose of extending the work to higher teperatures, however, that of applying cellulose hydrolysis to the field of refuse treatment and disposal, has still not been achieved; and of all the alternative refuse disposal methods mentioned in Chapter 2, acid hydrolysis and fermentation is perhaps the least developed. Fagan (1969) carried out the batch hydrolysis of two samples of ground refuse, and reported that the yield of glucose could be predicted by the same kinetic parameters obtained from the hydrolysis of kraft paper. Converse et al (1973) constructed a bench-scale plug-flow reactor to verify Fagan's results, but experienced considerable difficulties in maintaining steady-state conditions in their rig. The yields of glucose they obtained were generally low, and the only result of over 50% conversion was not repeated, as none of the reaction parameters could be set in advance with any certainty. As far as is known, this is all the work that has been done to date on the high-temperature dilute-acid hydrolysis of refuse.

The results of Converse et al (1973) were found to fit the kinetic model derived by Fagan (1969): these kinetic parameters were also used by Vaux and Santini (1975) to describe the results of their batch hydrolysis experiments with samples of newsprint. But the recent work of Thompson and Grethlein (1979) with a continuous reactor produced different kinetic parameters for the hydrolysis of newsprint; and quite different parameters again were obtained by Church and Wooldridge (1981) at slightly lower temperatures. These differences in the kinetic values reported need to be resolved, preferably by carrying out the hydrolysis of refuse in a continuous reactor under controlled conditions, and obtaining kinetic data.

The scope of the present work, therefore, which was aimed at obtaining such kinetic information, was set at:

(1) constructing a continuous reactor which would permit the hydrolysis of cellulose to be performed under previously determined, carefully controlled conditions. This would be done by modifying the existing rig at the University which had been specially built for this purpose, but which had never been made to work satisfactorily, and from which it had not proved previously possible to obtain kinetic data;

(2) carrying out the hydrolysis of filter paper as a "control" or model substrate, to establish the efficacy of the reactor and to obtain kinetic parameters to corroborate the work of Thompson and Grethlein (1979) with Solka-Floc (the only comparable work in the field);

(3) carrying out the hydrolysis of newsprint, which is a potential substrate for a commercial acid hydrolysis process, when using source-separated waste.

(4) carrying out the hydrolysis of refuse, to establish that this can be done, and to determine kinetic parameters to predict glucose yield.

(5) investigating the decomposition of glucose, to find out whether it does indeed follow a first-order reaction at high temperatures;

(6) using the kinetic values obtained from the experiments with refuse to draw up a preliminary plant design for a hydrolysis plant to produce ethanol from refuse, and to comment on the economics of the process.

This work is described in the next three chapters.

CHAPTER 4

EXPERIMENTAL EQUIPMENT - THE DEVELOPMENT OF A CONTINUOUS REACTOR

4.1 Introduction

When this project began, a continuous reactor for high-temperature cellulose hydrolysis had already been designed and constructed in the Engineering Mechanics Discipline of the Open University, and operated to produce hydrolysate for fermentation studies (Porteous and Anderson, 1980; Anderson, 1981). But as a result of persistent blockage problems, and difficulties with heating and temperature control, it had proved impossible to conduct experiments at the steady conditions required for obtaining reaction rate data. Consequently, major modifications were required before such a programme of controlled experiments could be undertaken.

This chapter describes the series of changes that were made in the gradual transformation of the rig from its initial to its present final form, which was used for collecting the experimental data presented in Chapter 5. A brief description of the original rig is followed by a discussion of the modifications that were made, and of the results of experiments performed at each stage in the development of the pilot reactor. A detailed description of the final version of the reactor is then given, together with the normal start-up and operating procedure, and the normal and emergency methods of shutdown. The product sampling method and the continuous recording of temperature at various points along the rig are also described.

Once all the modifications had been made, the rig had in effect been completely reconstructed: but the conceptual design and the logic of the process remained unaltered throughout.

4.2 Description and operating procedure for the original rig

The description of the original reactor starts with the raw material feed tanks, and proceeds through the experimental equipment in the order in which the feed flowed. A simplified diagram of the layout is shown in Figure 4.1.

Cellulosic material (either filter paper or newspaper) which had been previously shredded and ground to a particle size finer than 200 microns in a rotating knife mill, was weighed out and made up into a 0.1 or 0.2% slurry with distilled water in the slurry tank. This was a 45 litre stainless steel tank mounted over the pump inlet. An identical tank alongside held flushing water, which for the duration of these experiments was ordinary tap water.

At the start of a run, a measured quantity of sulphuric acid was added to the slurry in the slurry tank to make up the desired concentration. The acid was dispersed through the slurry, and the solid particles kept in suspension, by means of a variable-speed stirrer fitted to the lid of the tank.

Each tank was also equipped with an immersion heater. As may be seen from Figure 4.1, this rig was designed to raise the temperature of the slurry to the desired level in three stages, and the first stage of preheating was carried out in the feed tanks. Before the start of each run, the contents of both tanks were preheated to 90°C; flushing water was then pumped through the system until the desired operating conditions of temperature and pressure were reached in the reactor, and at that point the feed was changed over to acidified slurry.

The pump used in these experiments was a single-acting positive-displacement metering pump, the stroke of which could be varied from 0 to 100%, to give a flow rate of from 0 to 30 litres/hr through the reactor, at a maximum operating pressure of 3.45 MPa (500 psi). By varying the flow rate of the slurry its residence time in the reactor could be altered. On the delivery side of the pump, fitted into a manifold, were a pressure gauge and a presure relief valve, set to vent at 4.14 MPa (600 psi).

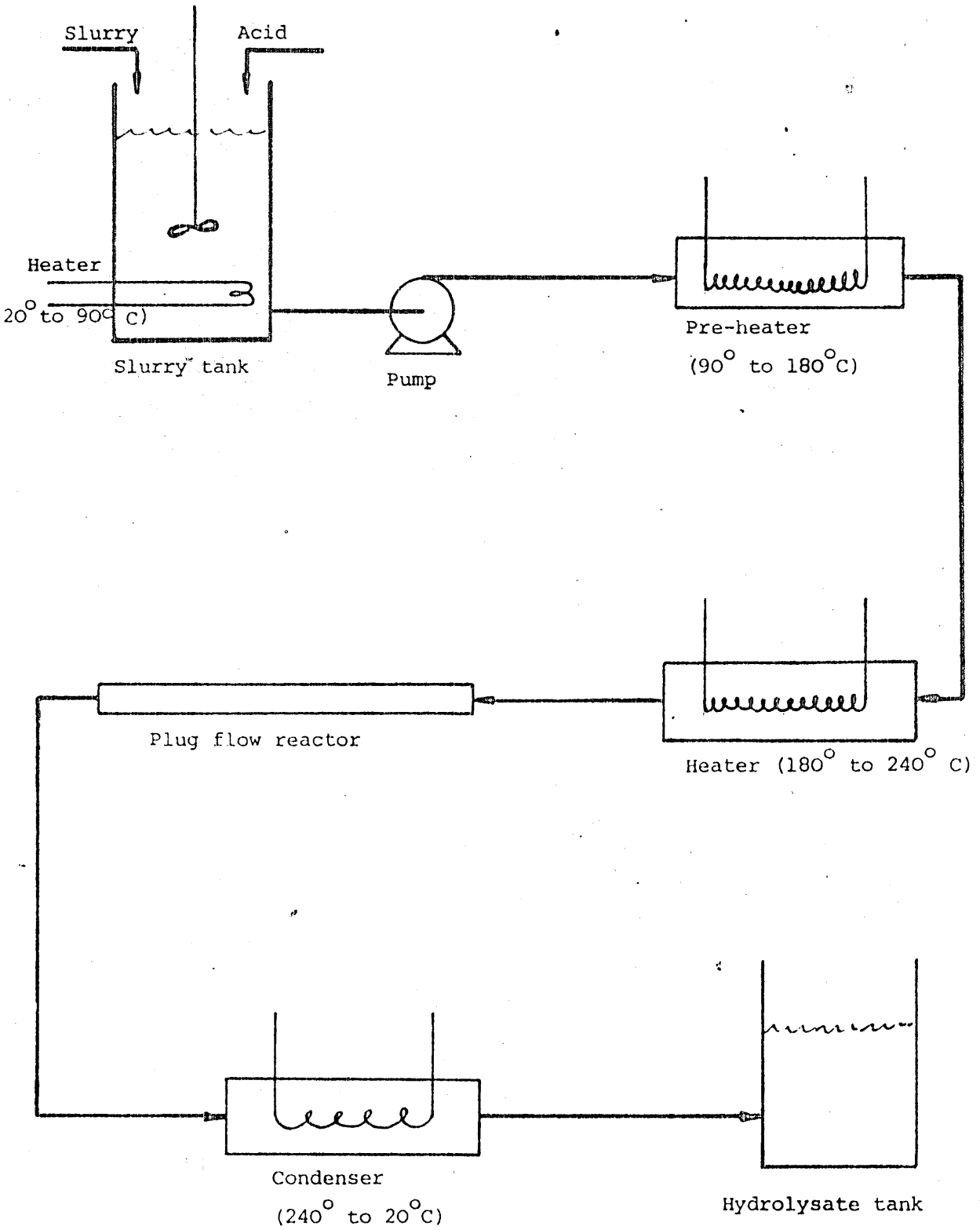


Figure 4.1. Simplified schematic diagram of Open University acid hydrolysis reactor - original rig.

The next major item of equipment was the "pre-reaction spiral", in which the second stage of preheating was carried out. This was a coil (2.5 turns) of 19 mm i.d. stainless steel tubing (316S), about 5.5 m in length, which was wrapped with electrical heating tapes having a combined capacity of 3.2 kW. In this section of the rig, the temperature of the slurry was raised from about 90° to about 180°C. The coil, wrapped with heating tapes, was contained in a well-insulated wooden box, filled with mineral wool.

From the preheater, slurry flowed into the "reactor", which was a 1 m length of the same 19 mm i.d. tubing. There was also a "second-stage reactor", this time two 1 m lengths of 19 mm i.d. tubing, connected together and to the reactor by means of U-bends. Both the reactor itself and the first "leg" of the second-stage reactor were wrapped with electrical heating tapes the purpose of which was to raise the final temperature of the slurry to a maximum of 240°C. Both reactor sections were placed in wooden boxes, those parts where heating took place being insulated with mineral wool.

The products of reaction left the second-stage reactor through a needle valve, which was also used to regulate the pressure in the system. The pressure downstream of the needle valve was atmospheric: the sudden pressure drop experienced by the hot solution on passing through the valve caused flash cooling of the hydrolysate, effectively quenching the reaction. The hydrolysate then passed through a condenser, which was a 6 m length of 9.5 mm (3/8") tubing, concentrically coiled and immersed in a tank of cold running water. Material leaving the condenser emerged at room temperature, to be collected, stored and analysed.

Between the reactor and the second-stage reactor was a manifold, to which was connected a line of 9.5 mm tubing going directly to the condenser, i.e. bypassing the second-stage of the reactor and the needle valve. A manually operated globe valve in this line could be opened in the event of a blockage occuring in the needle valve, and pressure rising suddenly in the reactor. A pressure bursting disk, rated to rupture at 4.66 MPa (675 psi) at 240°, was also connected to the manifold as an extra safety precaution; in the event of it bursting, the reactor contents were

vented outside the building into a sealed dump tank.

Slurry heating was controlled by means of three automatic temperature regulators, which set the temperature of the slurry leaving the pre-reaction spiral and the two reactor sections at 180° and 240° respectively. Temperature was measured at these points with the aid of thermocouple beads fastened to the outside wall of the tubing, and monitored on a mV meter calibrated to read in °C.

4.3 Early problems and resulting modifications

4.3.1 Blockaging

A very major problem with the rig, and one that had bedevilled trial runs by a previous researcher (Anderson,1981) was blockaging of the needle valve which served to regulate the pressure in the system. This valve was situated at the reactor exit, and needed only to be cracked open to set the pressure at 3.45 MPa (500 psi) when the temperature in the reactor was 240°C.

Because under "normal" operating conditions, the tapered needle was only slightly off its seat, the valve was easily blocked by any solid material remaining at the end of the reaction. Such blockaging would cause a sudden steep rise in the pressure in the reactor, necessitating the rapid opening of the manual by-pass valve, if the loss of a bursting disk was to be avoided. This usually signalled the premature end of an experiment, with the rig having to be left for several hours to cool down before the valve could be removed and unblocked.

These facts were confirmed during early work by the present investigator, who considered the set-up to be very unsatisfactory, as reliable operation of the rig was a practical impossibility, with the constant threat that the system would block up at any moment. Consequently, several alternative pressure-regulating devices were considered, to replace the needle valve, and the simplest and perhaps the most obvious choice was a fixed orifice. This allowed a bigger gap for

the solids to pass through for the same cross-sectional area. A range of fixed orifices was made up, of diameters varying from 0.35 to 0.60 mm, and they were tested on the rig in place of the needle valve. It was found that an orifice of 0.4 mm was the most suitable for obtaining a pressure drop of 3.45 MPa through the system when the temperature was 240°C.

Subsequent experimental work was thus carried out with a 0.4 mm fixed orifice in place of the needle valve. Blockages were still experienced from time to time, but on the whole, they were far less frequent and operation was generally much smoother, than with the needle valve.

The underlying cause of the blockaging could be put down simply to the small scale of operation - this was also the factor which limited the solid-liquid ratio in the slurry feed to less than 1%. A larger pilot plant with a higher throughput would not have required such a tiny constriction to create a back-pressure in the system. But a larger plant was impractical in the circumstances, as it would have required a bigger pump, larger storage facilities, and more heating than was available in the laboratory.

4.3.2 Reactor heating and residence times

Previous work with the rig had produced hydrolysates containing very low yields of glucose - Anderson (1981) reported only three runs in which the conversion of cellulose to glucose was greater than 5%. In 9 out of 14 runs, the conversion was 2% or less. The hydrolysates were dark brown to black in colour.

This suggested to the present investigator that hydrolysis was indeed taking place, but that the residence time of the slurry in the reactor and "second-stage reactor" was so long that the glucose formed was being completely decomposed on the prolonged exposure to acid at high temperature. This would explain the dark brownish colour of the hydrolysates, corresponding to the formation of 5-hydroxymethylfurfural followed by its polymerisation to humic substances (Newth,1951; Haworth and Jones,1944; Harris, Saeman and Zoch,1960).

Accordingly, the second stage of the reactor was removed, and the fixed orifice transferred to the outlet of the "first-stage" of the reactor. This effectively reduced the residence time of slurry in the system by approximately two minutes. At the same time, the heating tapes were removed from both reactor sections and added to the preheating coil, in an attempt to carry out the heating to high temperature in as short a time as possible. This was in order to approximate as closely as possible the ideal situation of instantaneous heating to the desired reaction temperature, followed by isothermal reaction.

A number of trial runs was performed, passing water only through the rig, to determine how much heating capacity was required on the preheating coil to raise the temperature from 80° or so to 240°C. It was found that a total of 4.4 kW of heating tapes was sufficient for this purpose, when the volumetric flow rate through the rig was about 15 or 16 litres/hr. The temperature was measured by thermocouples which had been moved from their former positions onto the 1 m long reactor section, one at each end and a third in the middle. The thermocouple at the reactor inlet (preheating coil outlet) was A, that halfway along was B, and the one at the reactor outlet, C.

Several runs were then carried out, using filter paper and newsprint as cellulosic feedstocks. The aim of these experiments was to operate the rig under steady state conditions, with the reactor temperature between 230° and 240°C, and to determine the extent of hydrolysis. Slurry concentrations were still kept low, at 0.3% or less, for fear of blocking the orifice, and the concentration of sulphuric acid was also kept below 0.3% as it was still thought that the residence time of slurry in the system was such that higher acid concentrations would have resulted in significant decomposition of the glucose product.

The progress of a typical run is shown in Table 4.1. The flushing water was preheated to 90°C before the start of the run; the newsprint slurry was preheated to 90°C while the rig was being brought up to temperature. After the pump had been switched on, the temperatures at points A, B and C were monitored continuously, and recorded manually at five minute intervals until the end of the run. As may be seen, about 50 minutes

Table 4.1

Progress of a typical run

time pm	temperature A	B	C	pressure psi	comments
2.00	24	24	24	--	
2.10	33	32	30	100	
2.15	52	51	50	240	
2.20	62	62	61	240	
2.25	68	68	68	260	
2.30	72	72	72	290	switched on heating tapes
2.35	102	100	98	330	
2.40	158	156	155	350	
2.45	186	185	183	390	
2.50	197	198	196	420	
2.55	203	202	201	440	
3.00	207	206	205	460	
3.05	216	214	213	430	
3.10	222	221	220	440	
3.15	226	225	224	460	
3.20	232	230	230	490	changed over to slurry
3.25	238	237	236	530	
3.30	240	240	240	500	flow rate: 16.35 litres/hr
3.35	239	239	239	490	
3.40	239	239	238	490	
3.45	239	238	238	500	flow rate: 16.35 litres/hr
3.50	239	239	239	500	
3.55	241	240	240	510	
4.00	241	241	240	515	switched heating tapes off changed to cold water flush
4.05	200	200	200	350	
4.10	158	160	172	300	
4.15	114	110	130	130	opened bypass valve - pressure dropped to zero, temp to 40°.
4.20					switched pump off

elapsed from the time the heating tapes were switched on until the temperature in the reactor reached 230°C.

At this point, the feed was changed from flushing water to acidified slurry. The temperature in the reactor rose after a little while, and then remained steady at about 240°C for about 30 minutes. During this time, the flow rate was constant at 16.35 litres/hr, and the temperatures at points A, B and C were for all practical purposes identical. Samples of hydrolysate were taken intermittently, making a total of over 5 litres, and the run was terminated when the level of slurry in the feed tank became too low. The hydrolysate samples were combined (for reasons explained in section 4.3.3 below) for glucose analysis by the method of HPLC (described in Appendix 1). The overall conversion of cellulose to glucose was found to be 15.4%.

A summary of the results obtained in this and other preliminary runs is shown in Table 4.2. These results were encouraging, as they showed that removing the two minutes of "reactor" residence time had had the desired effect, and that conversion of cellulose to glucose was definitely taking place. The heating and reactor sections had been separated, and operation under fairly steady state conditions had been achieved. The continuous hydrolysis of cellulose at elevated temperatures was being accomplished.

Numerous problems still remained, however. Although cellulose conversions to glucose of between 20 and 40% were being obtained, the hydrolysates were persistently dark in colour, indicating that significant decomposition of glucose was still taking place. So, before any more experiments were carried out, another alteration was made to the rig. The reactor section, consisting of the 1 m length of 19 mm i.d. tubing, was removed and replaced by a short (200 mm) length of 6.35 mm (1/4") o.d. stainless steel tubing. The aim was to reduce the residence time of slurry in the rig still further (by another minute or so) and so obtain higher yields of glucose, and permit higher concentrations of sulphuric acid to be used without resulting in excessive glucose decomposition.

Other changes had to be made as a result of using the smaller diameter tubing: the principal one was that the manifold which had been at the end

Table 4.2

Results of preliminary experiments

run no	slurry (% solids)	acid conc %	reactor conditions	cell conv %	comments
16	0.2% newspaper	0.15	239°C for 30 mins	15.4	cumulative sample of 5 l of hydrolysate
17	0.3% newspaper	0.28	237-242°C for 30 min	4.4	1 l sample from the cumulated hydrolysate
18	0.117% filter paper	0.1	233-236°C for 30 min	8.9	avg of duplicate samples from 1 l of hydrolysate
19	0.2% filter paper	0.1	234-236°C for 30 min	23.4	avg of 8 samples from 1 l cumulated hydrolysate
				39.0	instantaneous sample
20	0.26% filter paper	0.1	231°C for 10 min	18.6	inst. sample at 15.8 l/hr
				20.8	inst. sample at 16.2 l/hr
				13.9	inst. sample at 14.7 l/hr
				26.0	avg of 3 replicate samples of cumulated hydrolysate
				21.5	at 232°C and 260 ml/min
21	0.26% filter paper	0.1	232-239°C for 25 min	26.6	at 235°C and 270 ml/min
				32.2	at 236°C
				34.6	at 237°C and 280 ml/min
				33.8	at 239°C and 277 ml/min

of the reactor, and to which the bursting disk, fixed orifice and bypass line to the condenser had been connected, had to come away, and be replaced by a series of compression fittings, connected together by more of the 6.35 mm o.d. tubing (see Figure 4.2). This section of the rig was once again insulated by packing it with mineral wool,.but one of the advantages of replacing the bulky manifold and welded flanges with compression fittings and smaller diameter pipework was that heat losses from the system were reduced.

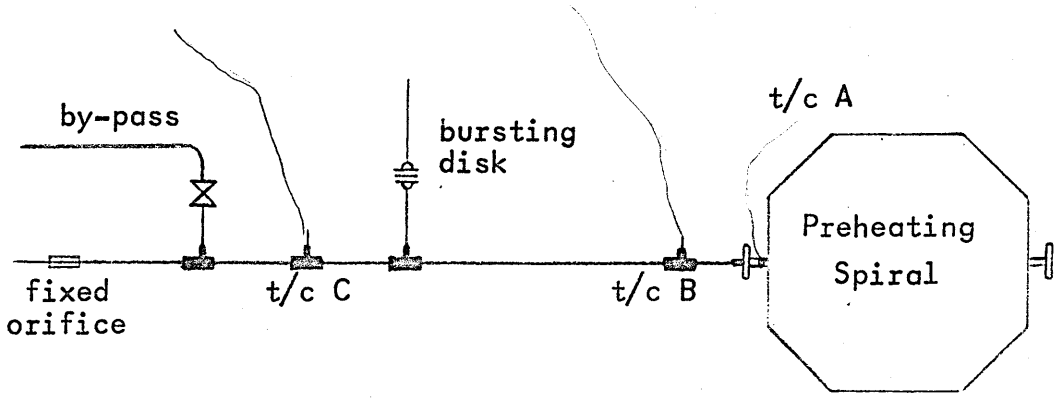


Figure 4.2. Layout of rig after replacement of reactor by smaller diameter tubing.

Another advantage was that compression fittings could be specially modified to permit thermocouple probes to be inserted directly into the slurry flow. This led to an immediate improvement in temperature measurement, and paved the way to swifter and more accurate temperature control. The (lack of) control of temperature was one of the main drawbacks of the preliminary experiments; the other was the method of analysis that was being used to determine the glucose content of the hydrolysates. These problems are discussed in the following sections.

4.3.3 Alteration of sampling and analytical technique

A very major problem encountered during the preliminary experiments was in the sampling and analysis of the hydrolysate product. Because of the very low concentrations of glucose in the hydrolysates, resulting from

the low solid-liquid ratios in the slurry feed, a lengthy procedure was required to prepare the samples for analysis. The actual determinations of the glucose content were carried out by a technician in the Chemistry Department, usng High Performance Liquid Chromatography (HPLC) to separate the sugars in the hydrolysates, and differential refractometry to measure quantitatively for glucose.

The method of preparation involved neutralising the hydrolysates with calcium hydroxide to pH 6 or 7, filtering out the calcium sulphate precipitates, and removing excess water from the samples in a rotary vacuum evaporator. All samples were reduced in bulk to less than 10 to 20% of their original volume. During the course of the evaporation, more calcium sulphate would be precipitated out of solution, and thus a series of filtration and evaporation steps had to be performed.

The procedure was very time-consuming, and it would often take a week or more to prepare the samples from a single run for analysis. Then, as the time of a technician in another department was involved, further delays could be experienced. Continuing with this method of analysis, therefore, would obviously have put a severe limitation on the number of experiments that could have been performed. Furthermore, the evaporation step necessitated the collection of large samples (or the combination of a number of duplicate samples) so that the number of individual samples that could be taken and analysed for each run was restricted.

The problem was circumvented by the acquisition of a YSI Industrial Analyser, which used an immobilised enzyme technique to analyse for glucose within 60 seconds. Because enzyme reactions are highly specific, interference from other sugars present in the hydrolysates was low. This method of analysis used very small samples (25 microlitres) and reproducibility was good, even at low concentrations of glucose (down to 0.01%). Using this method of analysis, therefore, it was possible to collect not only cumulative samples but many instantaneous or "spot" samples during the course of a run, and to monitor almost immediately the effect on glucose yield of varying the reaction conditions. This method of analysis for glucose was used for the remainder of the runs.

4.3.4 Temperature control and measurement

The preliminary experiments also highlighted the need for more accurate temperature control in the rig. The "on/off" temperature regulators used in conjunction with the heating tapes were found to be quite inadequate for maintaining the temperature at a preset level without large fluctuations. They would cut out at a temperature 10° to 20°C above the preset level, and allow the temperature to fall some 30° to 40°C before coming in again.

For the preliminary experiments, the configuration of heating tapes wound round the preheating spiral was fortuitously such that when they were all functioning at full capacity, the maximum temperature in the reactor reached 230° to 240°C, when the flow rate through the rig was 15 to 17 litres/hr. Consequently, the thermostats were set at 250°C during all these runs, rendering the controllers completely inoperative. In this way, it proved possible to carry out the experiments, but the situation was far from satisfactory, as there was no way of carrying out a hydrolysis at temperatures below 230° to 240°C short of removing one or more of the heating tapes, or replacing them with others of lesser wattage.

The reason for the poor operation of the temperature controllers can probably be ascribed to the wall thickness of the 19 mm i.d. tubing which comprised the preheating section. This would have made the response time relatively long. Stainless steel is not a very good conductor of heat, and it is likely that there was a difference of quite a few °C between the inner and outer walls of the tubing, especially when the temperature of the fluid passing through the tube was rising or falling.

To try and solve the problem, the on/off controllers were done away with and replaced by two "Variac" variable transformers, by means of which the voltage across the heating tapes and hence the temperature in the reactor could be set and controlled manually. This made it possible to operate the rig at temperatures from 190° to 240°C, although difficulties were experienced with fluctuations in the line voltage, which resulted in the temperature suddenly rising or falling in the middle of a run (see below).

As mentioned at the end of section 4.3.2., another alteration was made to the rig before the next set of experiments was carried out: the reactor section and the manifold were replaced by smaller diameter tubing and compression fittings. As a result of this, two of the thermocouple beads originally fastened to the outside wall of the reactor were replaced by thermocouple probes inserted into the slurry flow. These were thermocouples B and C; thermocouple A was moved to the end of the preheating coil, as shown in Figure 4.2. Like the beads, the thermocouple probes were of the nickel chromium/nickel aluminium type, and could thus be connected directly to the same mV meter, which was specially made for use with chromel/alumel thermocouples, and was calibrated in °C.

A series of 16 runs was performed with this new configuration. The aim was to try and operate the rig under steady state conditions at various temperatures between 180° and 240°C, and to determine the extent of hydrolysis. The acid concentration was varied from 0.1 to 1.0%, although most of the runs were carried out using 0.2 or 0.4% sulphuric acid. The substrates used were newsprint and filter paper. During two of the runs (Nos. 29 and 32) the bursting disk blew soon after the feed was changed over from flushing water to acidified slurry, and during two others (Nos. 36 and 37) blockages were experienced on the suction side of the pump on changing over the feeds. The results obtained from the other runs are shown in Table 4.3.

As may be seen, the maximum temperature in the rig, as measured by the thermocouples inserted into the slurry flow, was varied between 182° and 238°C during the filter paper experiments, and between 209° and 234°C when working with newsprint. Higher yields of glucose were obtained, under similar reaction conditions, than in the first set of preliminary experiments (cf Table 4.2). thus vindicating the replacement of the 1 m long reactor by the short length of smaller diameter tubing which effectively reduced the residence time of slurry at maximum temperature from one minute to a few seconds. Other interesting observations that can be made from the results in Table 4.3 are that higher conversions of cellulose to glucose (up to 70% and more) were obtained from the hydrolysis of newsprint than of filter paper (conversion being defined in both cases as the concentration of glucose in the hydrolysate as a

proportion of the cellulose content, expressed as potential glucose, in the feed); and that, in general, conversion increased with increasing temperature and acid concentration.

Table 4.3

Results of second series of preliminary runs

run no	slurry conc %	substrate	range of temps °C	acid conc %	conversion %	duration (min)
22	0.2	newsprint	214 - 233	0.2	30 - 70	60
23	0.2	newsprint	209 - 218	0.2	30 - 50	34
24	0.2	newsprint	210 - 220	0.4	36 - 78	51
25	0.2	newsprint	220 - 234	0.2	36 - 74	52
26	0.1	f.paper	193 - 224	0.2	6 - 36	50
27	0.2	f.paper	218 - 238	0.2	18 - 40	61
28	0.2	f.paper	212 - 230	0.4	20 - 34	62
30	0.2	f.paper	208 - 227	0.1	6 - 23	62
31	0.2	f.paper	182 - 207	1.0	8 - 28	53
33	0.2	f.paper	230 - 234	0.2	22	45
34	0.2	f.paper	225 - 233	0.4	24 - 38	43
35	0.2	f.paper	202 - 213	0.4	20 - 23	39

At the start of each run, the Variacs were set at a certain voltage depending on the desired initial temperature. When this temperature was reached, the feed was changed from flushing water to slurry. After a while, samples were taken, usually at one minute intervals, in disposable 5 ml test tubes. When a number of samples had been collected, the voltage on the Variacs was altered, and the temperature in the reactor changed accordingly. A certain time was allowed to pass for the system to reach a new set of equilibrium conditions, after which more samples were collected. Periodic checks were made on the flow rate - this usually varied between 15 and 17 litres/hr for all the runs. A run was terminated when the level of slurry in the feed tank became low, or when some problem was experienced, such as blockaging, or a heating tape burning out. The

length of time that slurry was passed through the rig during each run is listed in Table 4.3 as the duration of the run.

Two main problems were encountered during these experiments. The first was the difficulty in maintaining the temperature at a steady, preset level. Without the Variacs being touched, the temperature would suddenly rise or fall by a few °C in the middle of a run, and settle out at a new level. This was finally attributed to variations in the line voltage, which came about when other electrical machinery in the building was switched on or off. The other problem was in the scatter of the results. This undoubtedly had something to do with the first problem, but even when the temperature did remain constant for a few minutes, replicate samples of hydrolysate would often exhibit a difference of 10% or more in the extent of cellulose conversion observed.

The occurence of these two problems may be seen in a typical run, the progress of which is listed in Table 4.4. Both Variacs were set at 200V at the beginning of the run and when the temperature in the reactor reached 219°C, the feed was changed over to slurry. The temperature initially rose, but after 9 minutes settled at about 230°C, and sampling commenced. The temperature remained fairly steady for about ten minutes, and then suddenly dropped, to 225°C, and then to 221°C. Sampling was continued all the time, but after the temperature had fluctuated between 219° and 225°C for 13 minutes, the temperature was deliberately lowered further by reducing the voltage on the Variacs to 190V each. The temperature dropped to 214° to 215°C, then fell of its own accord to 210°C, and then the run was stopped on account of the orifice blocking up.

The reactor temperatures recorded during the course of this run are plotted in Figure 4.3. Also shown on the graph are the corresponding values of cellulose conversion. The scatter in these latter results is apparent, and is obviously not due only to the fluctuations in temperature. In fact, there is a rough similarity between the two curves in Figure 4.3,

Table 4.4

Progress of run 22

time pm	temperature A	B	C	pressure psi	glucose mg/dl	comments
1.30	22	22	22	--		
1.50	64	63	63	135		heating on both Variacs 200V
2.00	115	113	112	160		
2.15	148	147	146	190		
2.30	185	181	181	265		
2.40	198	194	194	310		flow rate: 16.2 l/hr
3.00	219	215	216	390		
3.05	222	218	218	410		
3.10	223	219	220	415		changed to slurry
3.15	226	223	223	445		flow rate: 16.6 l/hr
3.18	232	229	229	480		
3.19					15	sample 1
3.20	233	230	230	490	17	sample 2
3.21	233	231	231		21	sample 3
3.22					31	sample 4
					30	flow rate: 16.6 l/hr
3.24	233	230	230		42	sample 5
3.25	233	229	230	475	51	sample 6
3.26	233	230	231		59	sample 7
3.27	232	228	229		82	sample 8
					66	flow rate: 16.6 l/hr
3.29	233	229	230		77	sample 9
3.30	233	229	230	470	90	sample 10
3.31					86	sample 11
3.32	230	226	227	460	76	sample 12
					74	flow rate: 16.6 l/hr
3.34	230	225	227		76	sample 13
3.35	231	226	227	460	77	sample 14
3.36	230	225	227		85	sample 15
3.37	224	221	222		76	sample 16
3.39	224	221	222		69	sample 17
3.40	225	222	222	430	66	sample 18

Table 4.4 (continued)

time pm	temperature A	B	C	pressure psi	glucose mg/dl	comments
3.41	227	224	225		75	sample 19
3.42	229	225	226		83	sample 20
					94	flow rate: 16.2 l/hr
3.44	227	224	224		63	sample 21
3.45	225	222	222	430	125	sample 22
3.46	223	219	220		58	sample 23
3.47	224	222	222		59	sample 24
					63	flow rate: 16.5 l/hr
3.49	229	225	225		74	sample 25
3.50	226	222	222	235		cut Variacs back to 190V
3.55	218	214	215	395		
3.56	219	216	216		41	sample 26
3.59	218	214	215		42	sample 27
4.00	219	215	215	405	42	sample 28
4.02	219	215	215		48	sample 29
					46	flow rate: 16.3 l/hr
4.05	216	212	213	390	55	sample 30
4.06	215	211	211		42	sample 31
4.07	214	210	210	380	38	sample 32
					34	flow rate: 16.7 l/hr
4.09	215	212	212		40	sample 33
						orifice blocked - heating off, changed to flushing water

indicating that the yield of glucose is dependent on the temperature of hydrolysis. The scatter in the results which is not attributable to the temperature fluctuations may be appreciated from Figure 4.4, in which the conversion of cellulose to glucose is plotted against temperature. The points clearly demonstrate that cellulose conversion increases with increasing temperature: the results of run 23 are included in the same graph, to extend the data to lower temperatures.

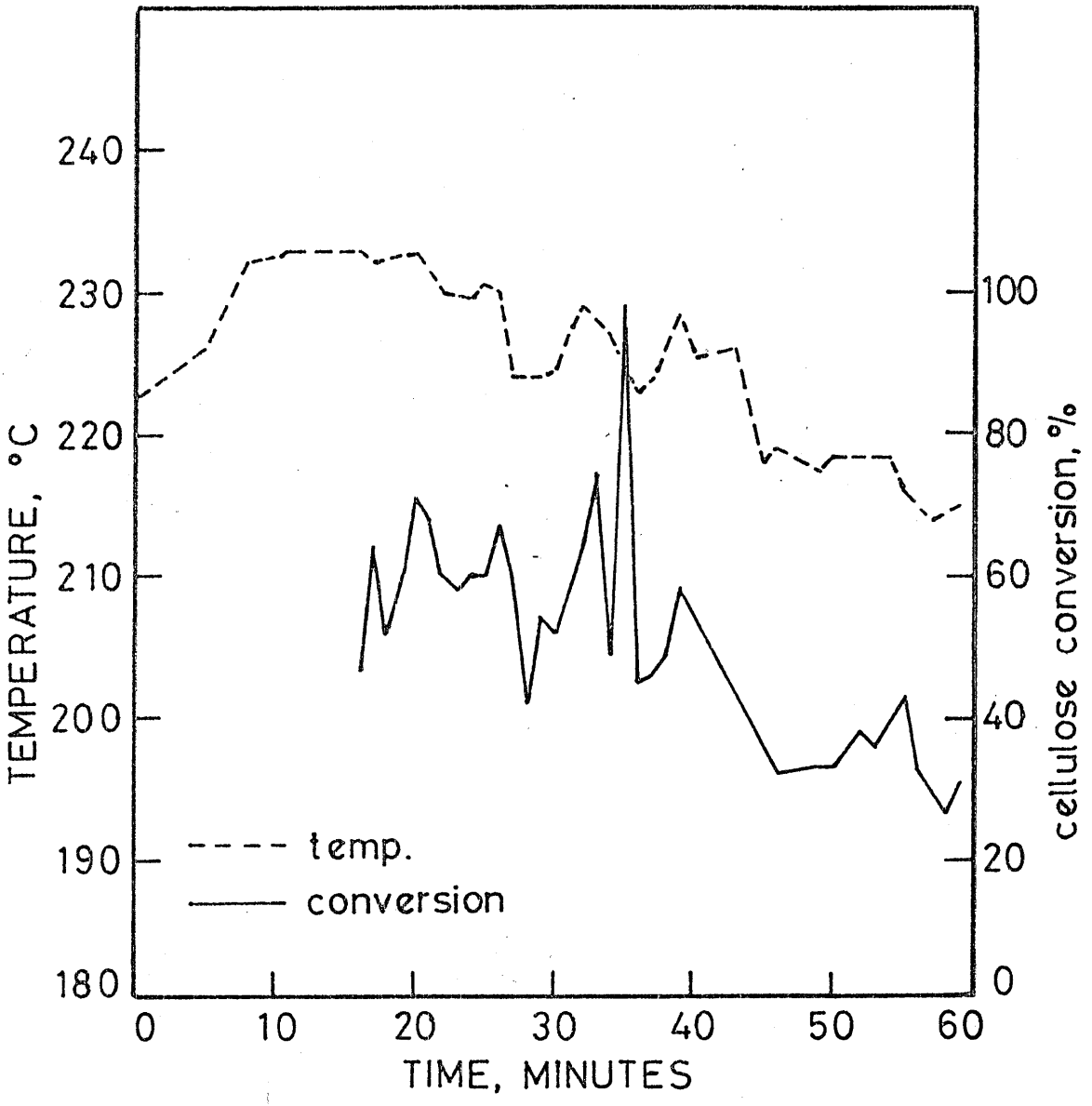


Figure 4.3. Progress of Run 22: variation of temperature and glucose yield with time.

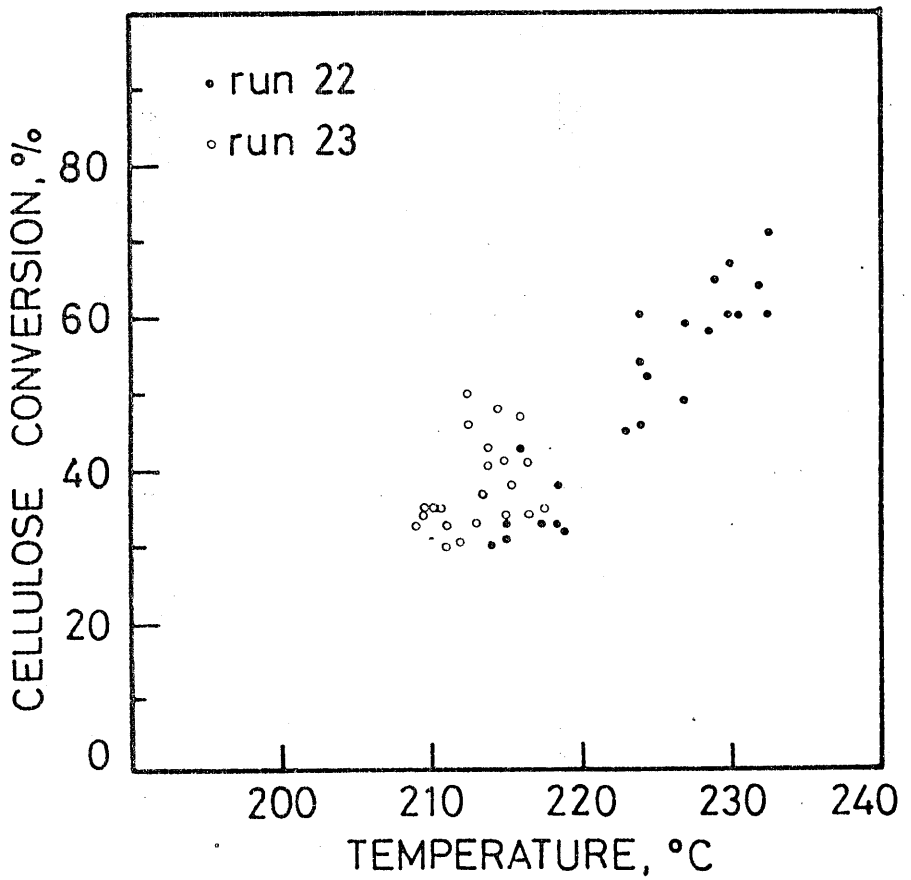


Figure 4.4. Variation of glucose yield with temperature, Runs 22 and 23.

Other results, obtained from experiments with filter paper at two different acid concentrations, are shown in Figure 4.5. These indicate that higher conversions are obtained when the hydrolysis is carried out with a higher concentration of acid - although, again, there is quite a large scatter in the results.

This problem of scatter in the data was attributed to experimental error, the fact that conditions in the rig were not steady. In particular, results like sample 22 of Run 22 gave a clue as to what was happening. A figure of 98% conversion was clearly impossible, especially when there was an inordinately large quantity of residual solids settled at the bottom of the test tube. This indicated rather that the flow of solids through the rig was uneven, but as the glucose content in the hydrolysates was always expressed as cellulose conversion in terms of the original slurry concentration (in the feed tank), such anomalies could occur. Many such instances did occur in this set of runs, and they were noticeable in a way

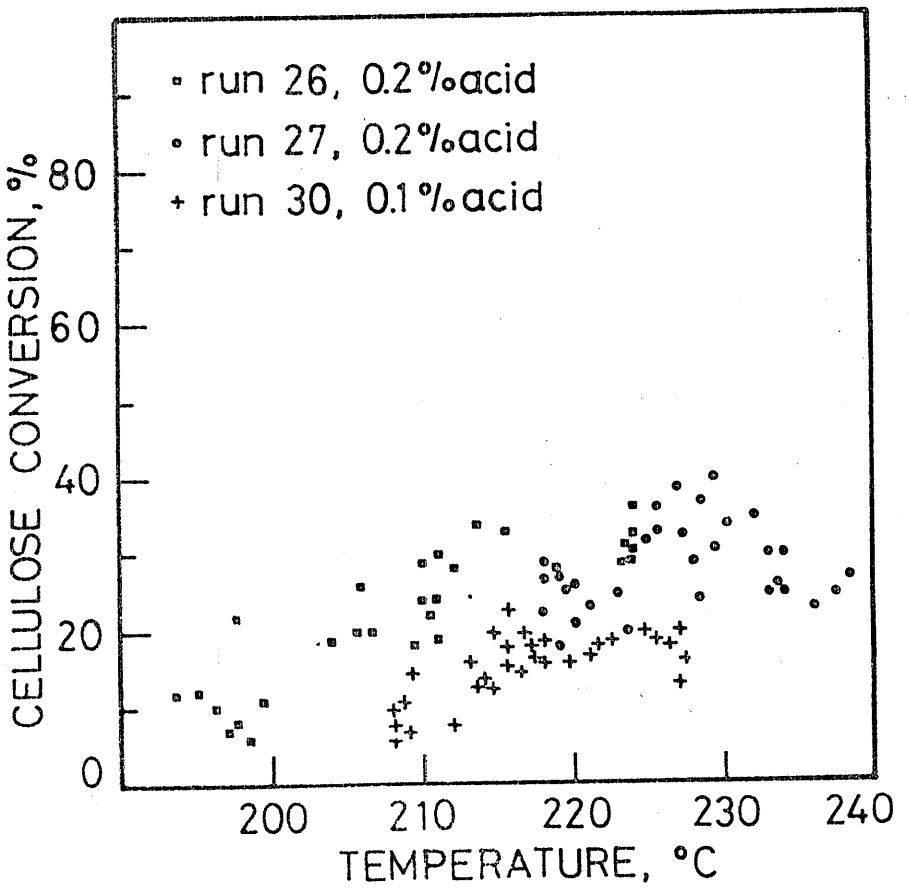


Figure 4.5. Variation of glucose yield with acid concentration.

they were not in the previous preliminary experiments, when large samples of hydrolysate had to be collected.

The cause of the uneven flow of solids through the rig was put down to the large diameter of the tubing in the preheating section. At a volumetric flow rate of 16 litres/hr, the flow in the 19 mm i.d. tubing was laminar, with a Reynolds number varying from 296 to 2083 as the temperature increased from 90° to 240°C (the calculations appear in Appendix 2). The linear velocity was only 2 cm/sec, and it was quite possible that some solid material was travelling through the rig in "clumps".

It was decided therefore to replace the preheating spiral with lengths of smaller diameter (6.35 mm o.d.) stainless steel tubing, wrapped with electrical heating cords. The internal diameter of this tubing was 4.52 mm, and the linear velocity of slurry through the new system was about 30 cm/sec, or 15 times as much as it had been through the large diameter

tubing. It was more likely under this circumstance that the flow of solids through the rig would be even; and indeed, the scatter in the results of duplicate samples, experienced during runs 22 to 37, was not encountered again. In subsequent work, agreement between as many as 10 different samples taken under the same reaction conditions was usually excellent, and there were no exaggerated differences in the quantities of residual solids which settled at the bottom of the test tubes.

Many other advantages ensued from the changeover to the small diameter tubing. The increased linear velocity of the slurry resulted in bigger Reynolds numbers, higher heat transfer coefficients, and a considerable improvement in the efficiency of heat transfer. With roughly the same wattage in heating cords as there had been heating tapes on the "pre-reaction spiral", the time required to raise the temperature of the same volumetric flow rate of fluid to 240°C was reduced to under 45 sec - without the necessity of any preheating in the feed tanks. Much smaller heat losses were also experienced from the smaller mass of heated tubing. The Reynolds number of slurry passing through the system now increased from 1244 to 8755 as the temperature rose from about 20° to 240°C. The increased rapidity in heating the slurry to the desired reaction temperature brought the system another step closer to the ideal of instantaneous heating followed by isothermal reaction.

Before changing over to this new system, an attempt was made to carry out the heating very rapidly, by constructing a heater consisting of six 1 kW infra-red heating elements arranged hexagonally around a straight length of 6.35 mm o.d. tubing. The tube was 0.6 m long, and the estimated residence time of slurry would have been only about 2 sec. Figures 4.6 and 4.7 are photographs of this radiant heating system, taken before and after the first and only time it was operated. It was found, in the event, that too much heat was lost to the walls of the heater and too little was transferred to the fluid flowing through the tube. An experiment with a conventional furnace heater, operated at up to 900°C, with the straight length of tubing passing through the middle of the heater, proved equally unsuccessful, and this work was abandoned. Work proceeded on a heating system consisting of small diameter tubing wrapped with heating cords, as described above.

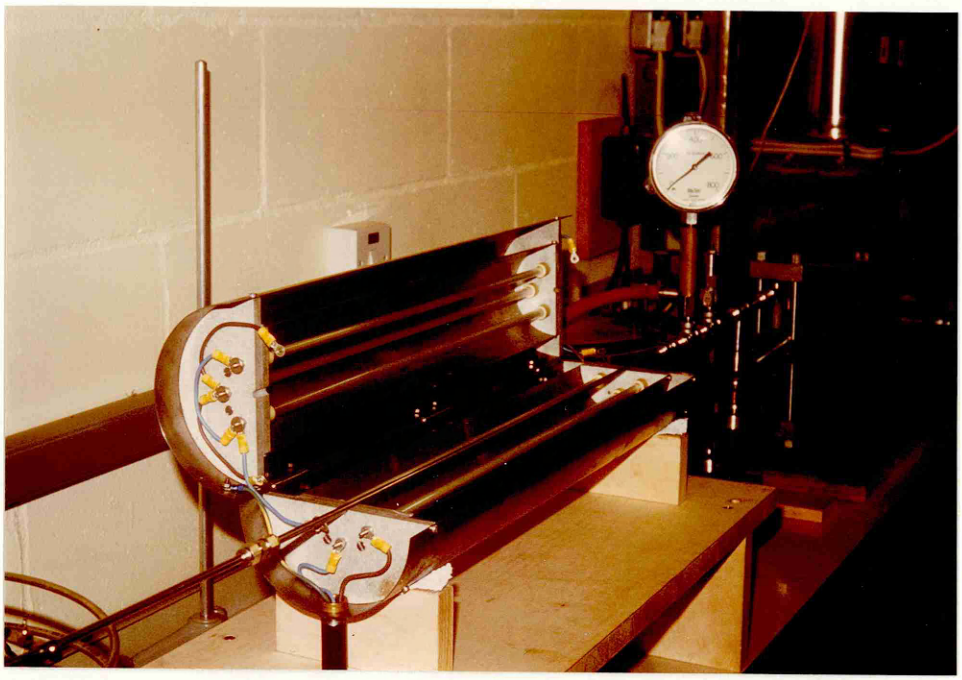


Figure 4,6. Slurry heating system using infra-red heating elements.

Figure 4,7. The infra-red heater after the first and only time it was used.

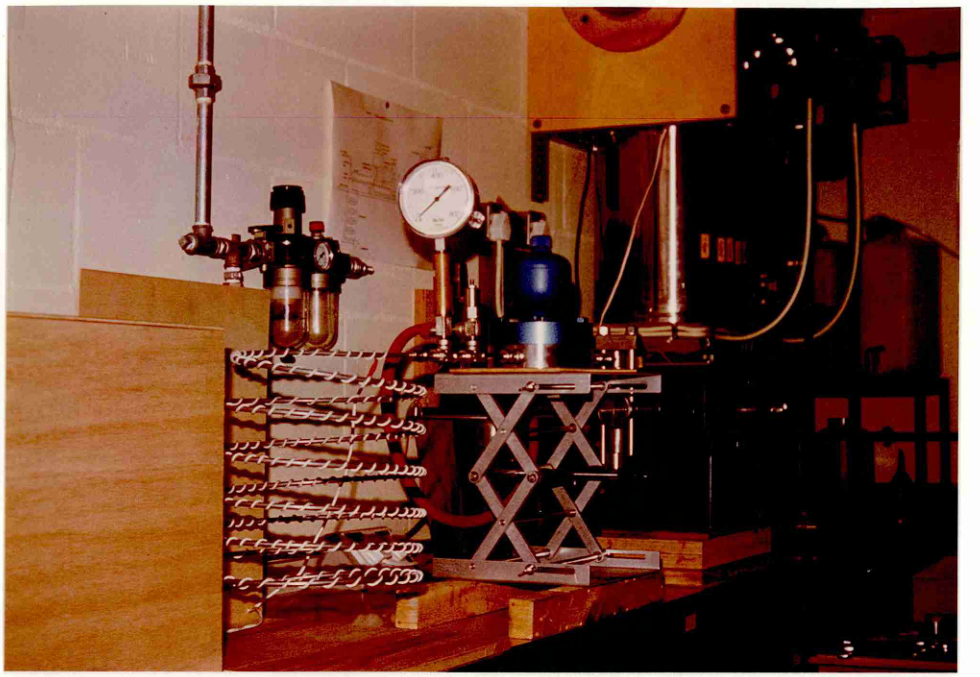


Figure 4.8. Photograph of modified rig showing feed tanks, pump, pulsation dampener, and one (of the two) preheating coils.

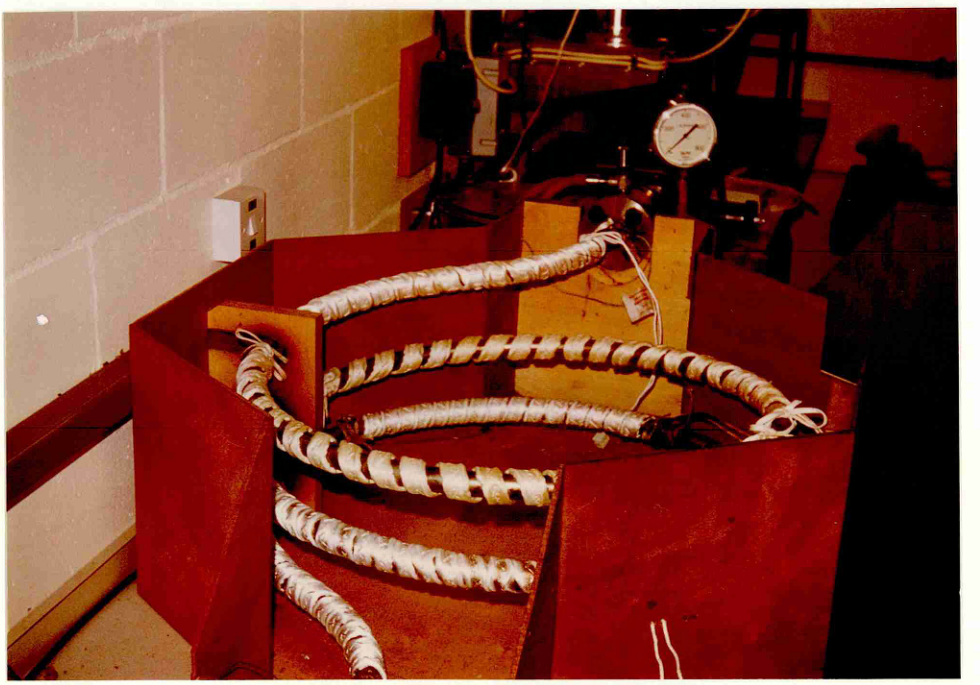


Figure 4.9. The "pre-reaction spiral" wrapped with heating tapes.

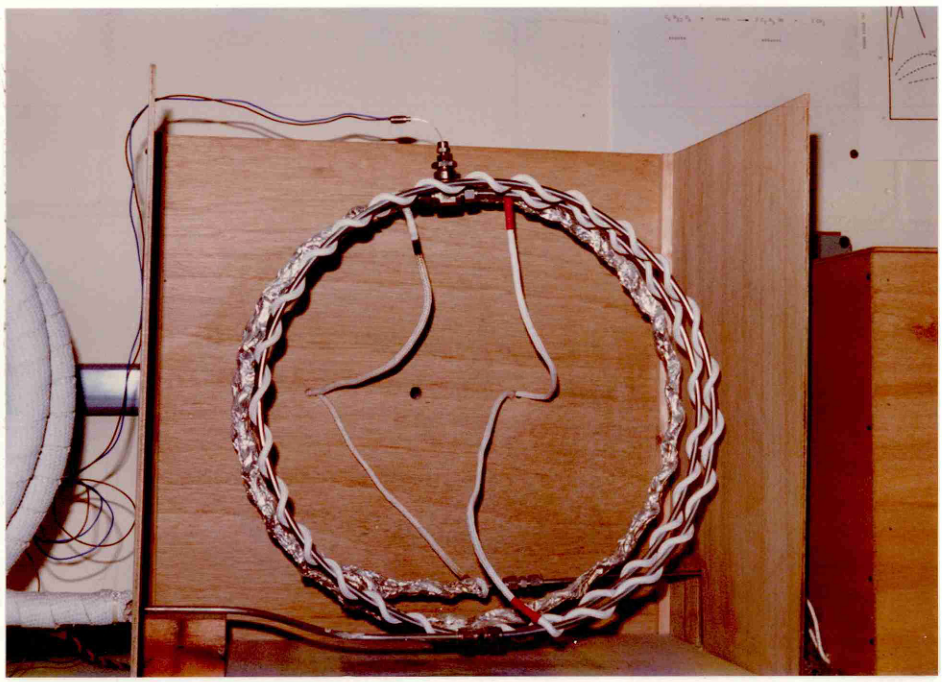


Figure 4.10. The final heating section of the modified rig.

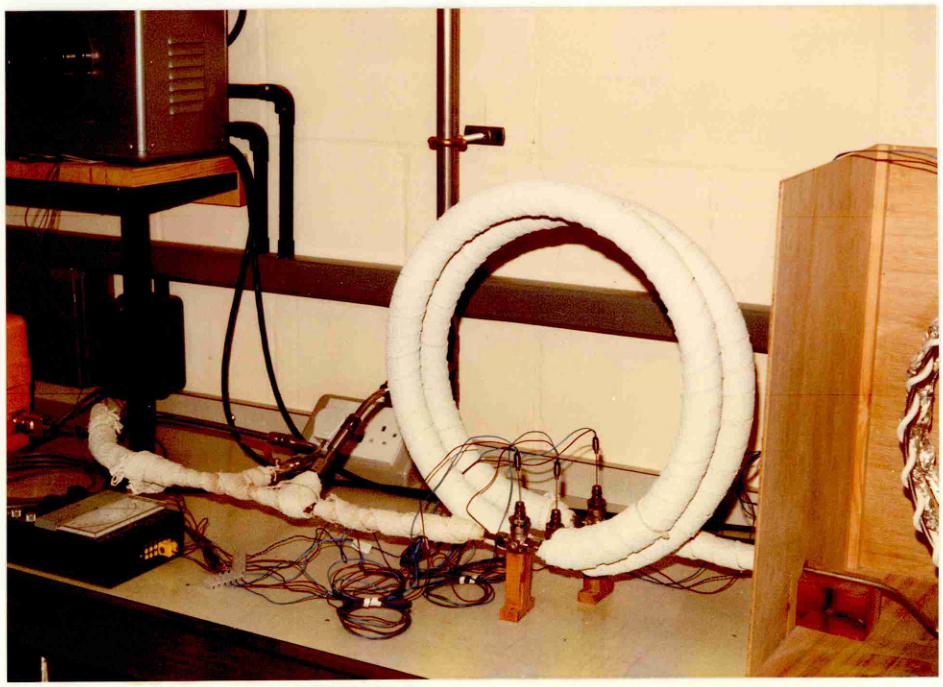


Figure 4.11. The reactor residence time coils, showing also the thermocouples, mV-meter, bursting disk and bypass valve.

The opportunity was taken, in designing the smaller rig, to revert to the original flowsheet in having a preheating section in which the temperature of the slurry was raised to about 180°C, followed by a final heating section in which the desired final temperature was achieved. The preheating section consisted of two helical coils having a combined length of 10.67 m, each wrapped with a 1.92 kW heating cord. The final heating section was made up of two 1.9 m lengths of tubing, each coiled and wrapped with an 800 W heating cord. Figure 4.8 is a photograph showing one of the helical preheating coils, wrapped with its heating cord, in its wooden box prior to packing with insulation material. The photograph also shows the feed tanks, and the pump and pulsation dampener, as well as the pressure gauge and pressure relief valve. Figure 4.9 is a photograph of the old large diameter pre-reaction spiral, for comparison; this is wrapped with a number of heating tapes. Figure 4.10 shows the final heating section, made up of two coils joined together, each wrapped by a heating cord; while Figure 4.11 shows the new reactor residence time coils which are described below.

The reason for wanting to separate the heating into two different stages again was not because of any problems experienced in heating the slurry or carrying out the experiments, but rather because of the difficulty in analysing the results. It was known, and confirmed during the second series of preliminary experiments (vide run 31 in Table 4.3) that cellulose hydrolysis begins to take place at an appreciable rate at a temperature of about 180°C. So, when the temperature in the reactor was 220°C (for example) the greatest part of the reaction was actually occuring as the slurry was being heated from 180° to 220°C; for the residence time of slurry in the "reactor", i.e. from the end of the preheating section to the fixed orifice, was very small (only 3 to 4 sec) compared with the several minutes that the slurry spent in the preheater between 180° and 220°C.

For exactly how long the slurry was at temperatures above 180°C in the preheating spiral, and what the temperature profile actually was during this time, was not known, partly because of the difficulty in obtaining accurate temperature measurements using thermocouple beads fastened to the outside wall of the large diameter tubing in places where the tubing

was being heated by electrical heating tapes, and partly because heat transfer to fluids in laminar flow is a very complicated process, as well as being inefficient. However, an accurate knowledge of the temperature-time history of slurry in the rig at temperatures above 180°C was crucial for the determination of kinetic parameters, as the rate of cellulose hydrolysis is so dependent on temperature.

Fortunately, the transfer of heat to fluids in turbulent flow is much better understood, and in addition another advantage of using smaller diameter tubing throughout was that it enabled more thermocouple probes to be inserted into the slurry flow to measure the temperature at all stages of the process much more accurately than had been possible with the thermocouple beads fastened to the outside wall of the large diameter preheating spiral. With the new rig, temperature was measured at the beginning, middle and end of the final heating section; and, as the heating cords provided heat at constant flux along the length of the small diameter tubing, it could reasonably be assumed that the rate of temperature increase in each of the 1.9 m coils was constant, i.e. that the temperature-time curve was linear. In any case, the residence time of slurry in each coil was so small (between 5 and 8 sec) that deviations in the assumed temperature-time profile would prove less serious when calculating the results.

Separating the heating of the slurry into two distinct stages also afforded the opportunity for further refining the control of temperature in the rig. The two Variacs were now used to control (manually) the heat supplied to the slurry in the preheating stage: feedback was provided by the thermocouple at the end of this stage which was monitored as a temperature reading on the mV meter. In the final heating section, automatic temperature control was provided, in the form of two electronic circuits, specially designed and assembled in the University's Electronics Workshop. These incorporated the use of triacs to regulate the voltage in each of the 800 W heating cords. The outputs from the thermocouples at the middle and end of the final heating stage were monitored and compared with settings which could be made on two potentiometers situated at the front of the control box. The response to changes in the preset levels was swift - the final temperature in the reactor could be increased or

decreased by 20°C in two to three minutes - and the control itself was very steady, usually varying by no more than 1°C above or below the preset level.

Because the Variacs were still being used to regulate the heat supplied in the preheating stage, variations in line voltage continued to affect the temperature at the end of this section of the rig. But this was at the lower end of the temperature scale. The use of automatic temperature controllers, coupled with the swift and accurate temperature measurement made possible by the use of smaller diameter tubing, meant that fluctuations in the final reaction temperature, which had been a problem in runs 22 to 37, were no longer experienced.

Having noted that most of the reaction in runs 22 to 37 took place in the preheating spiral, the fact that the heating time of slurry between 180°C and the final reaction temperature was now going to be reduced to between 10 and 16 sec (depending on the volumetric flow rate) meant that a proper reactor section was once again required to provide extra residence time for the hydrolysis reaction. It was also desirable that this residence time be variable, to enable kinetic data to be taken at a number of points during the course of the reaction. Reactor residence time, together with temperature and acid concentration, were the chief variables that were to be investigated for their effect on the extent and rate of cellulose hydrolysis.

Accordingly, the reactor section was made up of four equal lengths (1.21 m) of 4.52 mm i.d. stainless steel tubing, any number of which could be connected to each other by means of compression fittings to give multiples of a fixed unit of residence time. Each of these lengths was bent in a circle so as to make a coil when two or more were connected together. To minimise heat losses, and try and ensure isothermal operation, each coil was well insulated with a thick wrapping of asbestos tape (see Figure 4.11). Using this system, the length of the reactor and hence the residence time of slurry in the rig remained fixed throughout any particular run (barring fluctuations in the volumetric flow rate), but between one run and the next it was an easy matter to alter the reactor residence time by simply removing or adding one or more coils.

The simplest configuration of the rig was when no residence time coil at all was used - in the reporting of the results in Chapter 5, this is referred to as configuration number 1. The slurry was heated to the final reaction temperature, and resided in the system for the minimum of time, representing the distance between the end of the final heating section and the fixed orifice. Configuration number 2 refers to the system in which one residence time coil was used; number 3, two residence time coils; and so on. Thermocouples were inserted into the flow at the points where the residence time coils were connected to each other, so as to have a more accurate picture of the temperature profile over the entire course of the reaction. The temperatures measured by all the thermocouples were recorded continuously during each run using a Datalogger, which stored all the information on cassette tape.

One final change was made to the rig before experimental work was resumed, and that was to replace the plunger pump which had been in service since the original project was started. Blockage problems on both the suction and delivery sides had been experienced intermittently during the course of the preliminary experiments, which were put down to the design of the pump head, which included double ball valves on each side of the plunger. As it was hoped to carry out experiments with higher concentrations of slurry, an oscillating tube metering pump was obtained of the type used in industry to pump slurries such as suspensions of chalk and kieselguhr, and thick fluids such as yoghurt and marmelade. This was equipped with self-cleaning ball valves, one on each of the suction and delivery sides. Because, with the replacement of the pre-reaction spiral by the smaller diameter coils, the volumetric hold-up in the rig was so much smaller, it was found that a pulsation dampener was required for use with the positive-displacement pump. A compatible one was obtained from the same company which supplied the pump.

4.4 Modified plant description

This section describes each part of the rig in turn, beginning with the feed preparation equipment and going through the other items in the order in which the feed flowed. A schematic diagram of the modified rig is shown in Figure 4.12.

4.4.1 Feed preparation

A three-phase 1.5 kW rotating knife mill was used to reduce shredded filter paper, newspaper, or as-received air-classified lights to a particle size less than 200 microns. The mill had four stationary blades and three rotating blades (300 rpm). One kg of paper could be ground in approximately 30 sec.

4.4.2 Feed storage tanks

These were two 45 litre cylindrical stainless steel tanks mounted over the pump inlet, which held the slurry and flushing water respectively. The slurry tank was provided with a variable-speed stirrer fitted to the lid of the tank. The outlet lines from the two tanks were joined together with a "Y-piece" to form one inlet line into the pump.

4.4.3 Pump and pulsation dampener

An air-operated, positive-displacement, oscillating-tube metering pump was used, in conjunction with a diaphragm-type pulsation dampener. Both were manufactured by the Burdosa Company of Germany. The maximum operating pressure of the pump was 4 MPa; the delivery rate could be varied from 0 to 28 litres/hr by altering the frequency of stroking.

4.4.4 Preheating section

The preheating section consisted of two helical coils of 6.35 mm o.d. stainless steel tubing, around each of which was wrapped an electrical heating cord rated at 1.92 kW. Together, these were sufficient to raise the temperature of the incoming slurry from 20° to 180°C, below which the rate of hydrolysis is small. Each coil was placed inside a well-insulated

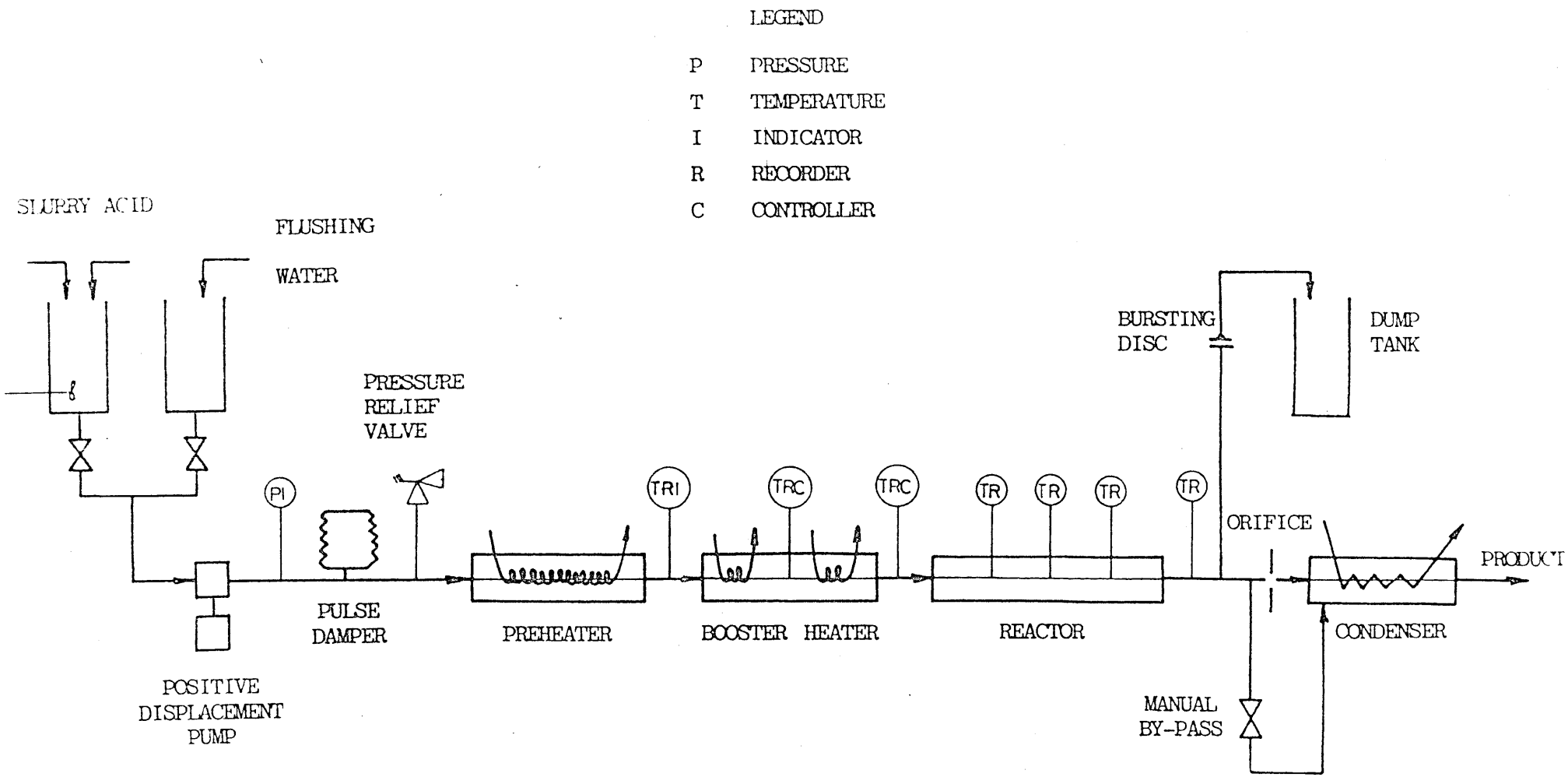


Figure 4.12. Schematic diagram of modified cellulose hydrolysis reactor.

wooden box, filled with mineral wool. The coils were connected to each other with compression fittings.

4.4.5 Final heating section

In this section of the rig, the temperature of the slurry was further raised from 180°C to whatever the final desired reaction temperature might be (up to 240°C). The heating was accomplished in one or both of two 1.9 m long stainless steel tubes, of internal diameter 4.52 mm and external diameter 6.35 mm. Each tube was coiled and wrapped with an 800 W electrical heating cord. This enabled each heating coil on its own to raise the temperature of the slurry by about 30° to 40°C, at a volumetric flow rate of 16.5 litres/hr. At this same volumetric flow rate, the residence time in each heater was 6.67 sec. The heating coils were placed in a well-insulated wooden box filled with mineral wool, and were connected to each other and to the rest of the rig with the aid of compression fittings.

4.4.6 Reactor section

The reactor section simply provided residence time for reaction. It was made up of none, one, two, three or four equal lengths of 4.52 mm i.d. (6.35 mm o.d.) stainless steel tubing which could be joined to each other with compression fittings to give multiples of a fixed unit of residence time (4.24 sec when the volumetic flow rate was 16.5 litres/hr). Each length measured 1.21 m and was bent into a circle so as to make a coil when two or more were connected together. They were all well insulated by wrapping them with asbestos tape.

4.4.7 Fixed orifice

The reaction products left the reactor through a fixed orifice of 0.4 mm diameter. This small diameter was required so that a pressure of 3.45 MPa (500 psi) could be maintained across the reactor when the temperature in the reactor was 240°C. The sudden pressure drop experienced by the hot solution as it passed through the orifice caused flash cooling of the hydrolysate, which effectively quenched the reaction.

4.4.8 Condenser

After passing through the orifice, hydrolysate entered the condenser, which was a 6 m coil of 9.5 mm (3/8") tubing immersed in a tank through which cold running water flowed. Hydrolysate emerged from the condenser at room temperature to be collected, stored and analysed.

4.4.9 Temperature measurement, recording and control

The heat supplied to the slurry in the preheating section was controlled manually by means of two "Variac" variable transformers, each of which was connected to one of the 1.92 kW heating cords. The heating of the slurry in the final heating section was controlled automatically with the aid of two electronic circuits which incorporated the use of triacs to regulate the voltage in the 800 W heating cords.

Temperature was measured at various points along the rig by thermocouple probes inserted into the slurry flow. This was done at points where sections of tubing were connected together, by using prefabricated tee-piece compression fittings which were specially adapted to hold the thermocouples. Figure 4.13 shows a cutaway diagram of one such thermocouple fitting. Thermocouples were positioned at the end of the preheating section, after each stage of the final heating section, and after each of the residence time coils.

The thermocouples were of the nickel chromium-nickel aluminium type. The readings from the two thermocouple probes situated after each stage of the final heating section were fed back to the automatic controllers which regulated the heating in this part of the rig, and hence the final temperature in the reactor. The readings from these and all the other thermocouples were monitored continuously during each run, using a Cristie Datalogger, which recorded all the readings onto cassette tape.

4.4.10 Safety

The rig was fitted with a number of safety devices in case of blockages which would cause sudden sharp rises in temperature and pressure. A pressure relief valve was situated on the delivery side of the pump (after

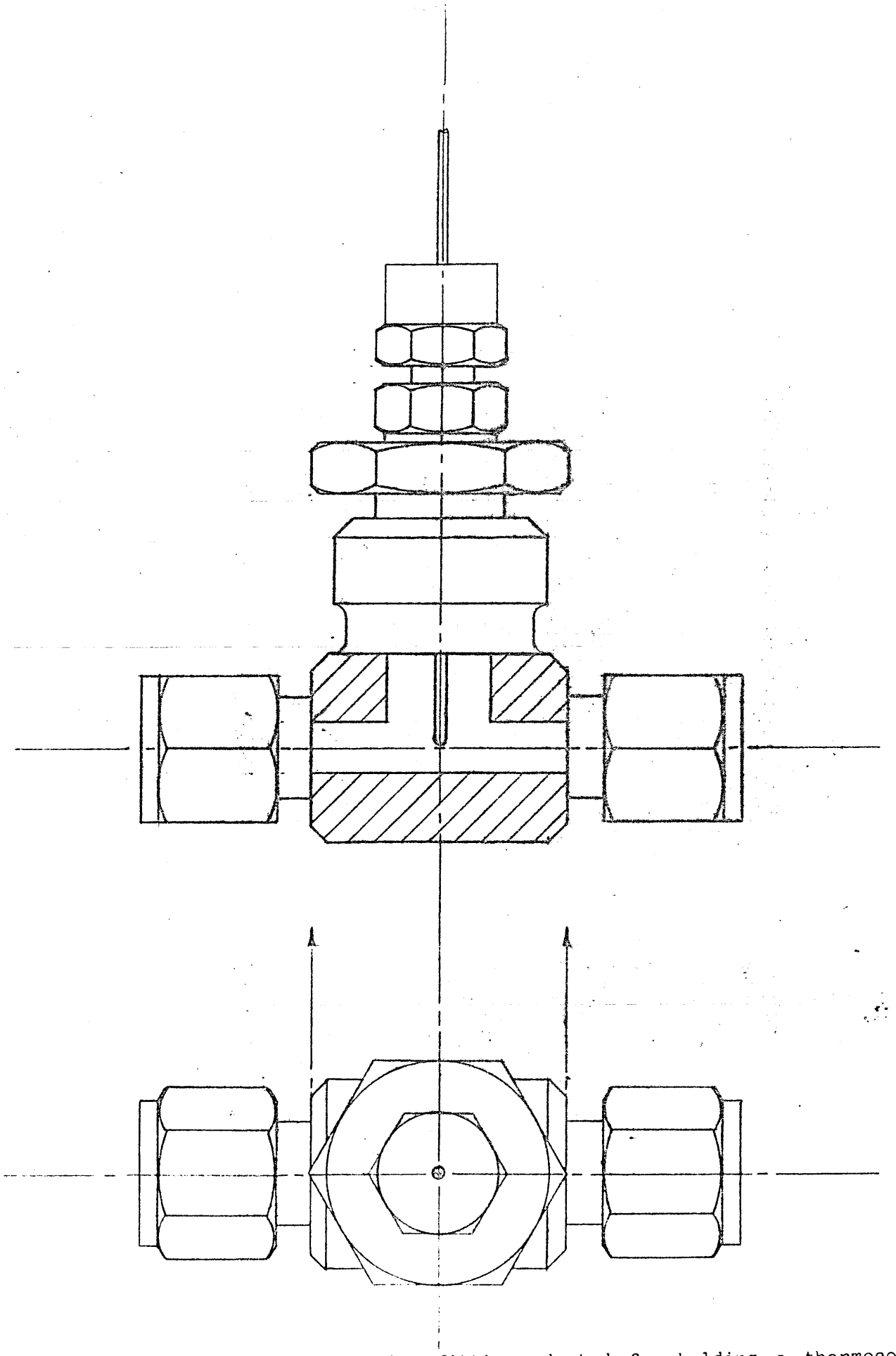


Figure 4.13. A compression fitting adapted for holding a thermocouple probe.

the pulsation dampener) and was set to vent at 4.14 MPa (600 psi). At the other end of the rig, just prior to the orifice, was a bursting disk which had been designed to blow at 4.66 MPa (675 psi) at 240°C. In the event of a disk bursting, the vapour would be vented into a pipe which led to a dump tank at the top of the building.

Just prior to the bursting disk was a manually-operated ball valve, which could be opened to release the pressure in the rig quickly, and allow flow to the reactor to bypass the orifice and proceed directly into the condenser. Finally, there was a circuit-breaker which cut off power to the Variacs if the temperature at the end of the final heating section exceeded 250°C.

The rig would always be run with another person in attendance: while the author directed the operation, and set the temperatures, took samples, etc, the other person (a technician in the Engineering Mechanics Discipline associated with the project) would keep an eye on the pressure gauge and a hand in the vicinity of the manual bypass valve in case of a sudden blockage occuring. Safety clothing was always worn, consisting of rubber aprons over laboratory coats, and face masks.

4.5 Operating procedure for the modified plant

Experiments with the modified rig were carried out in two stages, corresponding to feed preparation and actual operation. In order to eliminate blockage problems, samples of the cellulosic feedstocks were subjected to an initial size reduction process, consisting of shredding sheets of newsprint or filter paper in a commercial paper shredder, and grinding the shred in the rotating knife mill. Samples of refuse were ground without shredding, as they were obtained in a preshredded form. Size analyses of the final products showed that in each case, the particle size was under 200 microns.

The shredding and grinding operations were carried out at the beginning of each series of hydrolysis experiments, as the cellulosic feedstocks were investigated in turn. A sufficient quantity of finely ground material was produced to cover the anticipated requirements of all the

runs planned with that particular substrate. Then, before each run, a small quantity of the material would be weighed out and made into a slurry with a measured volume of distilled water in the slurry tank. Usually 30 or 60 g of ground filter paper, or 70 g of ground newsprint or refuse, were mixed with 30 l of distilled water. A calculated weight of concentrated sulphuric acid would be added to make up the desired catalyst concentration. This completed the feed preparation process.

Operations would begin by ensuring that the flushing water tank was filled with tap water. Flushing water was pumped through the rig at the start of each run, while the reactor and heating equipment were brought up to the desired operating temperature and pressure. The Variacs were used to set the temperature at the end of the preheating section to approximately 180°C, while the automatic controllers were adjusted until the temperatures in the reactor section were at the level desired for the first set of data. When the desired operating conditions were obtained, the feed was changed over to acidified slurry.

A few minutes were allowed to pass while the system reached steady state. Progress was monitored by keeping a watch on the temperature readings being recorded on the Datalogger, and noting the flow rate by measuring the volume of slurry collected from the reactor in a fixed time. When the conditions had remained steady for about five minutes, samples of hydrolysate were collected for analysis. A note was made of the exact time when each sample was taken, so that the temperatures at the various points along the rig at that time could be calculated from the information being recorded on the Datalogger.

After the hydrolysate samples had been collected, the system would be brought to a new set of operating conditions by altering the settings on the automatic temperature controllers. The response times were usually very swift, about two to three minutes, depending on the size of the increase or decrease in temperature. The system would be allowed to come to steady state once more, when more samples would be collected.The procedure was repeated several times during each run.

Each series of hydrolysis experiments, conducted with a particular cellulosic feedstock, investigated the effect on net glucose yield of varying three reaction parameters: temperature, acid concentration and reactor residence time. The temperature of hydrolysis was varied within each run, as has just been described. Changes in the acid concentration were made by varying the quantity of sulphuric acid originally added to the feed at the start of a run; or, alternatively, by temporarily suspending a run (by changing over to a feed of flushing water) after a set of samples had been taken over a range of temperatures at one particular acid concentration, and either adding more acid to the slurry or diluting it with distilled water. In either case, the stirrer motor would be switched off, and the volume of slurry remaining would be measured with a dipstick: a calculated quantity of distilled water or concentrated acid would then be added to bring the acid concentration to the new desired level. Changes in the reactor residence times had always to be made between runs, as this involved physically connecting or removing one or more of the residence time coils that made up the reactor section of the rig.

Normally, a run was brought to an end when the level of slurry in the feed tank became too low to continue, or when the desired number of samples had been collected. The feed would be changed over to flushing water, and the conditions in the rig maintained for about three minutes. This allowed most of the solids to be purged out of the system, and reduced the chances of blockaging. Then the temperature would gradually be brought down, by reducing the settings on the automatic controllers in stages to zero, and switching off the Variacs. Flushing water continued to be pumped through the system for a full 30 minutes after the temperatures had droppped below 50^{o}C, to cool the tubing down completely, and ensure that all vestiges of the run had been washed out of the system.

Four types of problems were experienced that occasionally necessitated the premature or abnormal termination of a run. This was when the orifice blocked with solids and the pressure and temperature in the rig began to rise suddenly and steeply; when acid corroded right through a piece of tubing (always in the final heating section) and caused a leak; when the bursting disk blew; or when the acid corroded either of the thermocouples

which provided feedback to the automatic controllers, making temperature control in the final heating section impossible.

Only the first two of these could rightly be called emergencies, in the sense that prompt action was required to prevent the situation deteriorating any further. Sudden and steep rises in the system pressure were countered in the first instance by opening the manual by-pass valve to release the pressure: all heating was switched off immediately, and the feed changed over to flushing water. If the pressure continued to rise, indicating that the by-pass valve was also blocked, the pump was also switched off and the system left to cool down by itself, over several hours. Acid corrosion through a piece of tubing was noticed by the inability of the system to come up to pressure during a run; the only way this could be corrected was by stripping down the final heating section and replacing the affected coil, and usually the heating cord as well.

4.6 Sample Collection and Analysis

At the start of each run, or whenever the slurry feed was changed (by dilution or acid addition) a sample was taken from the slurry tank for the determination of solids content (or glucose content) and acid concentration. While the run was in progress, samples of hydrolysate were collected either in a measuring cylinder over a fixed period of time (cumulative samples) or in 5 ml test tubes at equal intervals of time, usually 30 seconds (spot samples). The hydrolysate samples were analysed for glucose content, and residual solids or cellulose content. Glucose analysis was carried out using the YSI Industrial Analyser, while cellulose content was determined by the quantitative saccharification method. A description of these analytical methods appears in Appendix 1.

4.7 Summary

This chapter has described how through a series of preliminary experiments the original rig which had been designed and constructed for investigating the acid hydrolysis of cellulose was gradually modified so that it could be used to achieve its original purpose. This involved streamlining the rig by using smaller diameter tubing, to increase the flow rate of slurry through the system, and improve (and hence accelerate) the heat transfer; and decreasing the residence time to reduce the glucose decomposition. Significant improvements were also made in the measurement and control of temperature by using thermocouples inserted into the slurry flow and automatic controllers to set the final reaction temperature of the slurry.

The results of the preliminary experiments could not really be interpreted completely (i.e. to obtain kinetic data) because of inadequate control over the reaction conditions and insufficient information about several of the variables, in particular the residence time and the temperature-time history. However, it was observed that, in general, glucose yields increased with increasing temperature and acid concentration; and that higher conversions of cellulose to glucose were obtained from the hydrolysis of newsprint than of filter paper.

With the rig in its modified form, it was possible to carry out hydrolysis runs at steady-state conditions, monitoring the temperature constantly, and taking samples from which to obtain kinetic data. Four series of runs were carried out, with filter paper, newsprint, refuse and glucose as feedstocks. Details of the runs, and of the results that were obtained, are described in the next chapter.

CHAPTER 5

EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Introduction

The first objective of the present work was to modify the original rig to enable the hydrolysis experiments to be carried out under previously determined, carefully controlled conditions. This section of the work has been described in Chapter 4. Once these various modifications had been made, the rig was successfully operated for over 30 runs, for a total of over 17 hours, to obtain kinetic data about the hydrolysis of cellulose and the decomposition of glucose at elevated temperatures under the action of dilute sulphuric acid.

Four series of runs were carried out. The cellulosic feedstocks investigated were filter paper, newsprint and refuse; in addition, the kinetics of the decomposition of glucose were investigated. The experimental parameters that were varied were acid concentration, reaction temperature and reactor residence time. The aim of the experiments was to determine the optimum parameters for maximum glucose yield from the hydrolysis of the cellulosic materials, and to obtain kinetic parameters to corroborate the only other results that have been published of experiments carried out under roughly similar conditions, those of Thompson and Grethlein (1979).

In this chapter, the results of the experimental work are presented, and discussed. Each of the next four sections in turn describes the work conducted with one of the four substrates (including glucose). The effect of varying the acid concentration, temperature and reactor residence time are evaluated. Values of the kinetic parameters are obtained and compared with those of other researchers. The limitations of the present work are discussed, and suggestions made as to how these might be overcome. The

chapter ends with an overall evaluation of the experimental work, and the conclusions that might be derived therefrom.

5.2 Filter paper hydrolysis tests

5.2.1 Experimental programme and results

The first series of experiments used filter paper as a model substrate, to study in depth the kinetics of pure cellulose hydrolysis at elevated temperatures. From 17 runs, a total of 87 data points were obtained, each corresponding to a steady-state condition of the rig. Runs were carried out with 0.5, 1.0 and 1.5% acid concentration, over a range of temperatures varying from 205° to 240°C. The residence times were varied from 16 to 36 seconds, by using none to four residence time coils in the reactor section; these times include the residence time of slurry in the final heating section, where the temperature was over 180°C.

The detailed results of these experiments are listed in Appendix 3, in Table A.3.1. For each sample point, the following information is given:

(a) the run number (column 1).

(b) the configuration number (column 5). This refers to the number of residence time coils in the reactor section of the rig, according to the formula, configuration number = number of coils + 1.

(c) the acid concentration and solids content of the feed slurry (columns 2 and 3). These were determined from samples taken from the feed tank at the start of each run. Details of the analytical procedures, and sample calculations, appear in Appendix 4.1.

(d) The volumetric flow rate through the rig in ml/min at the time the sample was taken (column 4). This was determined by measuring the volume of slurry collected from the reactor in a fixed time.

(e) the temperatures in °C at various points in the rig at the time the sample was taken (columns 5 to 11). These temperatures were calculated from the readings recorded by the Datalogger during each

run, according to the method described in Appendix 4.3. The number of points at which temperature was recorded depended on the number of residence time coils in the reactor section during that particular run, i.e. on the configuration number. Temperatures A, B and C (columns 6, 7 and 8) always refer to the readings at the end of the preheating section, and the middle and end of the final heating section, respectively. For configuration number 1, when there were no residence time coils, temperature D (column 9) refers to the reading at the end of the short piece of tubing that was required to connect the end of the final heating section to the tail end of the rig. For the other configurations, temperature D is the measurement at the end of the first residence time coil, temperature E (column 10) at the end of the second, and temperature F (column 11) at the end of the third. When four residence time coils were used (configuration number 5) the temperature at the end of the last coil was not measured.

(f) the residence times of the slurry in seconds between various points in the rig, at the time that the sample was taken (columns 12 to 17). These were calculated from the measured value of the volumetric flow rate (column 4) and the calculated volumes of each of the lengths of tubing that comprised the rig (see Appendix 4.3). Values 1 and 2 (columns 12 and 13) are the residence times in the first and second stage of the final heating section, and are always equal as these stages were made from identical lengths of the same tubing. The other residence times are best described by approaching the rig from the other end, i.e. from the orifice back. The last value of residence time listed for each data point is the time taken for slurry to transverse the distance between the final thermocouple in the system and the orifice; the next-to-last value refers to the residence time between the last two thermocouples; and so on, back to the thermocouple at the end of the final heating section.

(g) the glucose concentration in the hydrolysate in mg/dl (column 19). This was the result of the analysis of the hydrolysate sample by the method described in Appendix 1.

(h) the net cellulose conversion to glucose (column 20). This was

calculated from the measured value of the glucose concentration in the hydrolysate (column 19) and the knowledge of the original cellulose content of the feed solids - for filter paper, this is 100%. A sample calculation (albeit for newsprint, whose cellulosic content was found to be 53.7%) appears in Appendix 4.2.

(i) the residual cellulose content in the hydrolysate (column 18). This is reported for the cumulative samples which were taken over a time interval of one minute. As filter paper is pure cellulose, the residual cellulose content was determined by filtering the solids, washing them thoroughly, and drying to constant weight in a recirculating air oven.

(j) the percentage of decomposition products in the hydrolysates (column 21). This was calculated by difference, as % decomposition products = 100 - (% residual cellulose + % cellulose converted to glucose).

(k) the type of sample (column 22). This states whether the sample point represents one cumulative sample collected over a time period of one minute, or the average of a number of instantaneous samples taken (usually) at 30 sec intervals when the conditions in the reactor were steady. Because the instantaneous samples were taken in 5 ml test tubes, it was not feasible to determine the residual cellulose content in these samples - thus only the glucose concentration and yield are reported.

The most interesting observations that may be made from Table A.3.1 are:

(1) the close agreement between the results of cumulative and instantaneous samples taken under the same reaction conditions. This indicates that the flow through the rig was even, and that solids were passing through the rig normally. It also shows that the automatic temperature controllers were functioning well, in maintaining steady-state conditions in the rig.

(2) the variation in temperature along the length of the rig. Reaction in the rig is non-isothermal. The temperature rises sharply to a maximum in the final heating section (thermocouples A to C) and then

falls away slowly in the reactor residence time coils (thermocouples D to F). With the heating being non-instantaneous, it would have been more satisfactory had the temperature in the reactor section been isothermal. But this was not the case. Some heat was still lost through the wrapping of asbestos tape wound around the reactor residence time coils. The insulation would have been better had these coils been placed inside a wooden box filled with mineral wool, but this would have made changing over from one configuration to another much more complicated. For ease of operation, it was decided to tolerate the drop in temperature, to measure the temperatures exactly, and to account for the variations in temperature in the calculations.

(3) the variation in the flow rate during the course of a run. It was found that the volume of slurry delivered by the pump would change automatically during a run, when the temperature was increased or decreased. The pump was designed to deliver a fixed volume against a certain working pressure: but as the temperature in the reactor was altered, so the pressure changed too. Usually the flow rate would decrease slightly as the temperature increased. Sometimes the flow rate was deliberately changed, usually in order to obtain higher temperatures when working with the rig at configuration numbers 4 or 5, when the heating cords were stretched to their limit.

The detailed results in Table A.3.1 are set out in chronological order, as the runs were made. A summary of these results appears in Table 5.1. Each row represents one of the data points in Table A.3.1, but duplicate results have been omitted, and data points at very similar conditions are represented by only one result. In order to make the Table more comprehensible, the results are grouped together according to the configuration number of the rig, i.e. in order of increasing residence time, going down the Table. Within each group, the results are further subdivided, into groups of increasing acid concentration. Each of these little groups normally represents one run, and the results are tabulated in order of increasing temperature.

Table 5.1

Summary of filter paper hydrolysis results

run no	con fig no	acid conc %	temperatures A	B	C	D	E	F	cell conv %
52	1	0.5	168	194	227	217	---	---	7.5
52	1	0.5	174	202	236	225	---	---	12.2
53	1	1.0	167	197	222	220	---	---	18.2
53	1	1.0	176	213	234	233	---	---	30.6
54	1	1.0	195	220	240	240	---	---	40.1
66	1	1.5	171	205	223	222	---	---	26.4
66	1	1.5	179	213	233	232	---	---	42.7
51	2	0.5	178	208	224	224	---	---	16.9
51	2	0.5	190	221	227	233	---	---	24.5
51	2	0.5	193	226	232	238	---	---	30.7
55	2	1.0	178	212	222	212	---	---	25.0
55	2	1.0	189	226	230	223	---	---	34.0
65	2	1.5	168	203	222	216	---	---	29.5
65	2	1.5	169	206	231	224	---	---	45.0
65	2	1.5	169	206	233	227	---	---	47.7
50	3	0.5	175	209	228	226	221	---	18.8
50	3	0.5	193	231	236	236	238	---	27.3
60	3	1.0	166	182	218	211	206	---	19.6
60	3	1.0	170	184	224	217	213	---	25.4
62	3	1.5	161	193	219	213	207	---	26.3
62	3	1.5	163	201	226	220	214	---	34.3
56	4	0.5	171	202	219	218	217	211	11.7
59	4	1.0	175	186	214	209	206	200	19.9
59	4	1.0	176	200	227	222	219	212	30.0
70	4	1.5	177	214	216	213	207	201	29.0
70	4	1.5	181	217	226	225	224	218	39.0
70	4	1.5	189	225	233	233	234	233	45.0
57	5	0.5	180	200	219	213	211	+++	13.9
57	5	0.5	181	212	227	225	221	215	20.9
58	5	1.0	174	195	209	204	201	+++	16.6
58	5	1.0	176	200	216	210	207	+++	20.9
58	5	1.0	176	203	224	219	216	+++	27.5
69	5	1.5	176	211	212	209	203	197	23.0
69	5	1.5	179	215	223	223	222	217	32.0
69	5	1.5	178	215	224	224	223	218	35.0

It may clearly be seen from the Table how the glucose yield increases with increasing acid concentration, temperature and residence time in the reactor. It is also possible to notice that the glucose yield goes through a maximum, as the residence time is increased for the same temperature and acid concentration, though more work at higher temperatures would be required to demonstrate this clearly. It in fact proved difficult when working with configuration 5 especially to operate at the highest temperature, even after reducing the flow rate and setting the automatic temperature controllers on maximum: the problem was no doubt due to heat losses from the residence time coils, which would obviously increase with the number of coils.

For clarity, the acid concentrations of the data points listed in Table 5.1 are nominally reported as 0.5, 1.0 and 1.5%. It will be seen from Table A.3.1 that this approximation is very reasonable, as the measured acid concentration in the feed slurries was never more than 3% from the desired value (except in run 64, when there was a miscalculation in the amount of acid that needed to be added to the slurry! - but this run is not reported in Table 5.1). The glucose concentrations measured in the hydrolysates revealed a net conversion of cellulose to glucose varying from less than 10 to over 45%. The highest yields were obtained with 1.5% acid concentration at a temperature of 233°C - the highest value of maximum temperature attained during these runs. When operaing the rig at configuration number 1 under these conditions (run 66), the conversion of cellulose to glucose was 42.7%; with configuration number 2 (run 65), 47.7%; and with configuration number 4 (run 70), 45.0%. These three results also indicate that the net yield of glucose goes through a maximum as the residence time of the reaction is increased, with other conditions remaining (approximately) the same.

The results obtained from the hydrolysis of filter paper when running the rig at configuration numbers 1, 3 and 5 are also plotted, in Figure 5.1. For each point, the temperature plotted is the maximum measured in the rig at the time that the sample was taken. The increase in glucose yield with increaing temperature, or acid concentration, is evident. The effect of increasing residence time is not so apparent, but it may be found by, for example, reading off the curves for 1.0% acid the net yield of glucose at

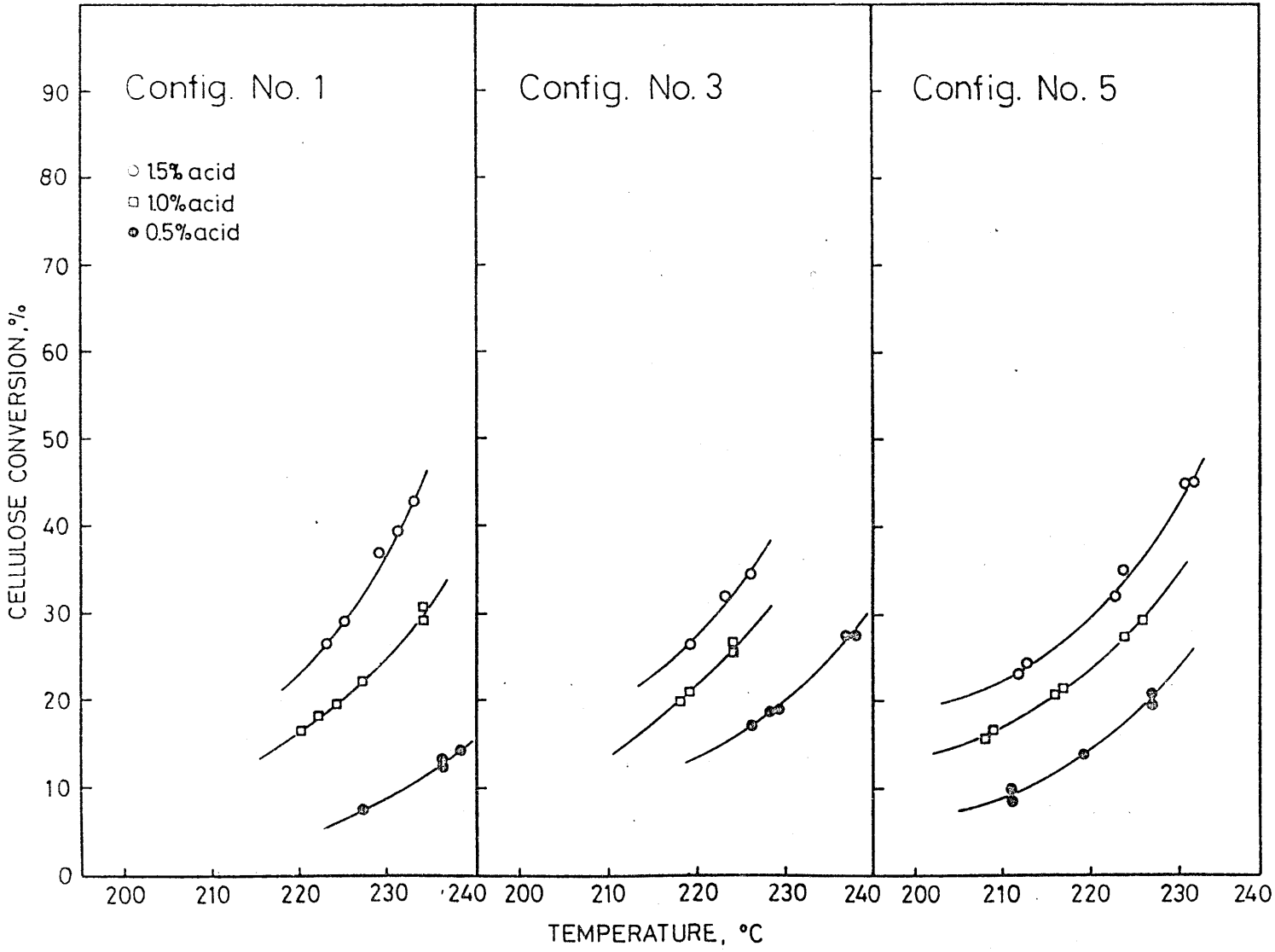


Figure 5.1. Variation of glucose yield with temperature, acid concentration and residence time (configuration number) for filter paper hydrolysis.

225°C at each of the three configurations: 20.0% at configuration number 1, 26.7% at configuration number 3, and 28.2% at configuration number 5. The yield of glucose therefore increases with increasing residence time, but with diminishing returns.

5.2.2 Estimation of kinetic parameters

One of the aims of this work was to obtain kinetic parameters to corroborate the work of earlier researchers. The kinetic model chosen to describe the results, therefore, was the usual one, that of Saeman (1945), which is discussed in detail in section 3.4. The conversion of cellulose to glucose by hydrolysis is represented by the consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \text{..... equation 5.1}$$

where k_1 and k_2 are first-order reaction rate constants, related to the isothermal reaction temperature and acid catalyst concentration according to the expressions

$$k_1 = P_1 \cdot C_a^m \cdot \exp^{-E_1/RT} \qquad \text{..... equation 5.2}$$

$$k_2 = P_2 \cdot C_a^n \cdot \exp^{-E_2/RT} \qquad \text{..... equation 5.3}$$

where C_a is the sulphuric acid concentration in weight percent, R is the universal gas constant, T is the absolute temperature, E_1 and E_2 are activation energies, and P_1, P_2, m and n are empirically derived constants (see equations 3.2 to 3.9).

The differential equations for a reaction system of two first-order consecutive reactions have been seen to be (equations 3.5 and 3.6)

$$dC_A/dt = -k_1 C_A \qquad \text{..... equation 5.4}$$

$$dC_B/dt = k_1 C_A - k_2 C_B \qquad \text{..... equation 5.5}$$

For constant temperature and acid concentration, equations 5.4 and 5.5 can be integrated to produce an expression for the glucose yield as a function of reaction time (equation 3.9); but as the filter paper hydrolysis tests were conducted under non-isothermal conditions, a

numerical integration for the glucose yield had to be carried out instead, with the yield as a function of temperature and time, and temperature as a function of time. The temperature was assumed to vary linearly between points in the rig where the temperature was measured: this was a reasonable assumption, as in the final heating section the heating cords provided heat at constant flux along the length of the small diameter tubing, so the rate of temperature increase could be said to be constant; while in the reactor residence time coils, the change in temperature was generally quite small, so any deviations from the assumed temperature-time profile would not prove serious when calculating the results.

The numerical integration was carried out using a Runge-Kutta technique, and assuming values for the parameters in equations 5.2 and 5.3. The empirically derived values of P_1, P_2, m, n, E_1, and E_2 reported by Saeman (1945), Fagan at al (1971) and Thompson and Grethlein (1979) were used in the first instance, and the predicted glucose yield for each data point was compared with the experimentally determined value. The sum of squared deviations was used to estimate the closeness of fit. The computations were performed on the University of Cambridge IBM 3801 computer, using a programme which incorporated the RUNGK subroutine available in the standard NAG library. The programme is listed in Appendix 5.

The results of these computations are shown in Table 5.2, which indicates that of the three sets of previously derived parameters, agreement is closest with those of Thompson and Grethlein (1979). All three sets of parameter values give estimates of glucose yields that are on average higher than the experimentally determined values (sigma negative) with the results predicted by Fagan's parameters showing the greatest deviation. It was found that by modifying the Thompson and Grethlein parameters slightly, a better correlation was obtained; this is the last column in Table 5.2. This set of parameters underestimates the glucose yields slightly, but it is an improvement both in terms of the sum of the deviations and the sum of the squares of the deviations.

Table 5.2

Kinetic model parameters for cellulose hydrolysis

parameter	Saeman (1945)	Fagan et al (1971)	Thompson and Grethlein (1979)	suggested by this work
P_1, min^{-1}	1.73×10^{19}	28×10^{19}	1.22×10^{19}	1.22×10^{19}
m	1.34	1.78	1.16	1.16
E_1, cal/mol	42900	45100	42500	42750
P_2, min^{-1}	2.38×10^{14}	4.9×10^{14}	3.79×10^{14}	3.79×10^{14}
n	1.02	0.55	0.69	0.69
E_2, cal/mol	32870	32800	32700	32800
SUM OF DEVIATIONS	-5.059	-9.688	-2.875	0.684
SUM OF SQUARED DEVIATIONS	0.701	2.053	0.375	0.177

5.2.3 Discussion

The results of the experimental programme with filter paper showed that the rig could indeed be operated under controlled conditions to obtain data which could be used to evaluate kinetic parameters; and that the kinetic parameters so derived were in good agreement with the only other values which have been obtained from cellulose hydrolysis work at such high temperatures in a continuous reactor, those of Thompson and Grethlein (1979).

Experiments were carried out at three acid concentrations, varying from 0.5 to 1.5%: a significant improvement was noted in glucose yield as the acid concentration was increased, at all residence times studied. As the residence time was increased for the same temperature, however, by connecting additional residence time coils, the glucose yield appeared to go through a maximum, and then to drop. More work at the longer residence times and at high temperatures would be required to demonstrate this clearly, but in the present work it proved difficult to obtain the desired high temperatures at the longer residence times.

Unfortunately, although isothermal reaction was desirable both in order to obtain higher glucose yields and to simplify the calculations, it was not possible to operate under these conditions. In the circumstance, the heating was made as rapid as possible by using the small diameter tubing and high-wattage heating cords, and allowance was made for the temperature variation by accurate measurement of the slurry temperature at a number of points during the course of the reaction (along the length of the rig) and using a numerical integration to estimate values of the kinetic parameters.

The glucose yields obtained were very reasonable, nonetheless; the highest value of cellulose to glucose conversion obtained was 47.7%, operating with Configuration No. 2 (residence time 20.4 sec, including heating time) and using 1.5% acid at a maximum temperature of 233°C. Values of 40% glucose yield were also obtained when using 1% sulphuric acid, at a temperature of 240°C, and a total residence time of about 19.5 sec (Configuration No. 1). High conversions of cellulose to glucose

could be obtained repeatedly by operating at 1.5% acid and high temperatures.

It was concluded from the results of this work that the rig in its modified form could be used quite validly to investigate the hydrolysis of cellulosic materials, and to obtain kinetic data. This was especially so as the kinetic parameters of Thompson and Grethlein (1979) had been corroborated, on the basis of a large number of data points (87). Many of these data points were duplicates of cumulative samples and of the average of a number of samples collected at fixed time intervals: the excellent agreement between these duplicate samples confirmed that it was possible to operate the rig under the controlled steady-state conditions required for collecting rate data.

5.3 Newsprint Hydrolysis Tests

5.3.1 Experimental programme and results

Five runs were carried out using milled newsprint as feedstock, and with the rig at configuration numbers 1, 3 and 5. During three of these runs (87, 88 and 89) the feed slurry (and hence the acid concentration) was diluted at a certain point during the run, so in effect hydrolyses were carried out at three different acid concentrations for each of the three residence time variations. As with the filter paper, the acid concentrations used were 0.5, 1.0 and 1.5%, while the temperature was varied between 199^{o} and 236^{o}C. The maximum slurry concentration used was 0.214%. The feedstock was actually sheets of old "Daily Mail" newspapers, which were shredded and milled to a particle size finer than 200 microns (see Appendix 6 for a size analysis of this and the other cellulosic feedstocks).

The detailed results of these runs are listed in Table A.3.2 in Appendix 3. A total of 31 different data points were obtained each corresponding to a different steady-state condition of the rig. The same information is given for each sample point as in Table A.3.1 for filter paper - except that for selected samples, residual cellulose was measured by quantitative

saccharification of the residue (as described in Appendix 1.2), and expressed as a percentage of the potential glucose content of the feed.

Problems were experienced with the Glucose Analyser during this stage of the work: in fact, a whole set of runs (Nos 71 to 82) was lost because the glucose values in the hydrolysate were inexplicably high, representing over 100% conversion, and the readings drifted as the sample was analysed and dropped with time (even after a few minutes). The actual cause of the error was never identified, although it was found (eventually) that by neutralising the hydrolysate and letting the precipitate settle, the glucose readings were steady and reproducible, even after 24 hours and more. It did not matter whether the neutralisation was carried out with calcium or sodium hydroxide: the final glucose readings were the same. Among the precipitates were hydroxymethylfurfural, which is known to come out of solution as the pH is raised, and some of the products of hemicellulose hydrolysis, and their decomposition products. Solutions of mannose and xylose (the chief products of the hydrolysis of hemicellulose in British newsprint, which is made from spruce) were made up and tested for interference on the Glucose Analyser, but this was found to be negligible.

It is thought that the interference might have been due to some other product of hemicellulose hydrolysis, or to some chemical in the newsprint, perhaps in the ink. When consulted, the U.K. distributors of the Glucose Analyser could not offer any enlightenment: they merely stressed that as the analysis relied on an immobilised enzyme assay, all interferences would be expected to be minimal. For the rest of the work, all samples of hydrolysate were neutralised with 1 N NaOH prior to glucose analysis. This meant that all the samples from then on were "cumulative" samples.

The results of the newsprint runs are set out in an abbreviated form in Table 5.3. There are three groups of results, each of which corresponds roughly to one set of temperaures. Within each group, the results are further subdivided according to the configuration number of the rig, and the acid concentration. As may be seen, the glucose yield increases with increasing acid concentration, temperature and residence time. Cellulose conversion was high, reaching over 70% at the highest temperatures. The

Table 5.3

Summary of newsprint hydrolysis results

run no	con fig no	acid conc %	temperatures A	B	C	D	E	F	cell conv %
86	1	1.5	174	208	216	214	---	---	46.9
87a	1	1.0	171	207	217	216	---	---	42.9
87b	1	0.5	173	210	215	214	---	---	31.6
89a	3	1.5	174	209	214	208	202	---	49.7
89b	3	1.0	173	208	216	211	206	---	51.4
90	3	0.5	176	210	215	210	205	---	41.0
88a	5	1.5	177	212	215	215	213	209	52.9
88b	5	1.0	193	218	217	217	217	217	54.6
88c	5	0.5	190	218	217	217	217	218	45.4
86	1	1.5	179	214	227	226	---	---	62.2
87a	1	1.0	174	209	226	226	---	---	52.7
87b	1	0.5	176	214	224	224	---	---	39.3
89a	3	1.5	177	212	226	220	213	---	64.9
89b	3	1.0	177	212	224	218	213	---	61.3
90	3	0.5	183	215	226	221	216	---	48.0
88a	5	1.5	184	219	223	223	223	221	63.7
88b	5	1.0	195	225	226	226	226	226	70.2
88c	5	0.5	200	224	223	223	223	223	55.9
86	1	1.5	183	218	236	235	---	---	71.3
87a	1	1.0	183	218	235	236	---	---	69.6
87b	1	0.5	185	222	236	236	---	---	57.5
89a	3	1.5	179	214	234	228	222	---	69.7
89b	3	1.0	182	217	235	233	228	---	72.6
90	3	0.5	190	218	234	234	231	---	55.0
88a	5	1.5	201	230	230	231	231	231	70.3
88b	5	1.0	203	231	231	231	231	231	74.3
88c	5	0.5	201	228	227	227	227	227	63.8

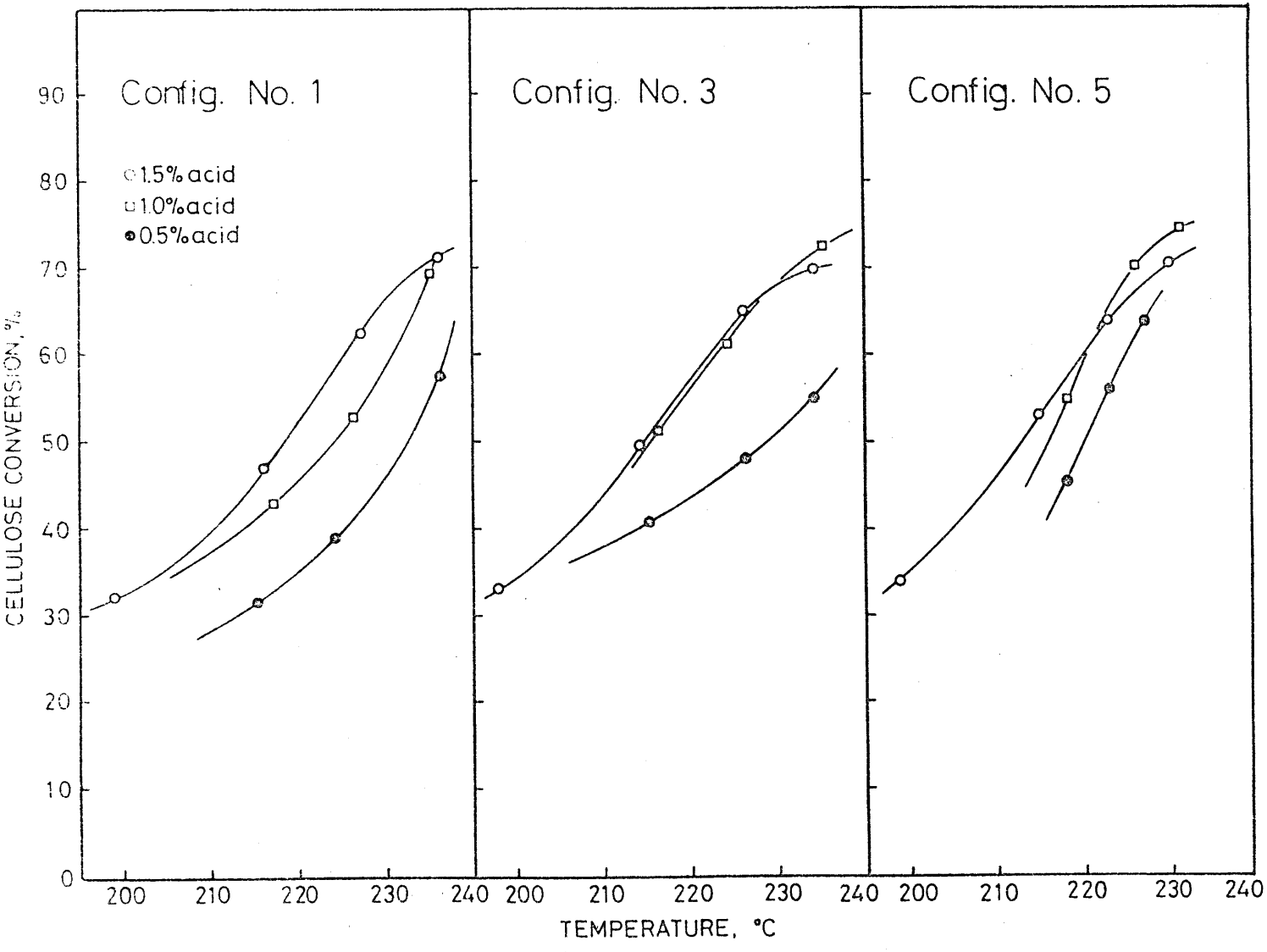


Figure 5.2. Variation of glucose yield with temperature, acid concentration and residence time (configuration number) for newsprint hydrolysis.

highest value obtained was 74.3%, when operating with configuration number 5 (total residence time 38 sec) at a temperature of 231°C, using 1% sulphuric acid. Other values over 70% were obtained when operating with 1.0 or 1.5% acid at temperatures of 226°C or higher.

The results are plotted in Figure 5.2. As in Figure 5.1, the maximum temperature is plotted for each sample point. The increase of glucose yield with increasing temperature and acid concentration is obvious, and it may also be seen how the results at 1% acid gradually overtake those at 1.5% acid with increasing residence time, indicating that the conversion goes through a maximum. More work at higher temperatures or longer residence times would be required in order to demonstrate this clearly.

5.3.2 Estimation of kinetic parameters

The same numerical integration method described above (section 5.2.2) was used to predict values of glucose yield for each of the data points for assumed values of the kinetic parameters. These values were compared with the experimentally determined values, using the sum of squared deviations to measure the closeness of fit. In the first instance, the published parameters of Saeman (1945), Fagan et al (1971) and Thompson and Grethlein (1979) were used, but none of these sets of values fitted the data. It was found that agreement improved in all cases if C_{AO} was taken as 0.9 and C_{BO} as 0.1 - this is equivalent to assuming that 10% of the cellulose is originally in an easily hydrolysable (amorphous) form, and that it is converted to glucose instantaneously at 180°C, which is the point at which reaction was assumed to start. A value of $C_{BO} = 0.1$ was also used by Fagan et al (1971) to describe the hydrolysis of kraft paper, while Thompson and Grethlein (1979) used $C_{BO} = 0.04$ to account for the more accessible portion of cellulose in Solka-Floc.

Another correction was made, for temperature. As may be seen from Table 5.3, it was not possible during all the runs to keep the temperature at the end of the preheating section to 180°C or less. This was especially so at the longer residence times (Configuration Nos 3 and 5) and the higher temperatures, when extra heating was required. This fact was taken into account in the computer programme to predict glucose yield,

by calculating the point along the preheating coils at which the temperature reached 180°C, and adding another heating stage to the calculations, in which the temperature increased from 180°C to whatever the temperature was at point A.

Even with this correction, the previously determined kinetic parameters did not fit the data, so a search was made for new values which would allow a fit to the general model without departing any further than necessary from the previously determined ranges. The values which were found to give the best fit were

$P_1 = 1.22 \times 10^{19}$ min^{-1}
$m = 0.7$
$E_1 = 41900$ cal/mol
$P_2 = 3.59 \times 10^{14}$ min^{-1}
$n = 0.0$
$E_2 = 33\,330$ cal/mol

Using these values, the sum of the deviations was 0.588 and the sum of the squares of the deviations 0.147. The values were found by trial and error, by starting with the Thompson and Grethlein (1979) parameters and varying each parameter in turn until a set of predicted values was obtained which was closest to the experimental values. A computer programme was written to do this for all six variables simultaneously, using a simplex search method, but the programme took too long to execute on the Cambridge computer. It is likely that other values of the parameters can be found that fit the data equally well, and it is not certain whether the set of values found is indeed the best.

Examining the values more closely, and comparing them with all the previously derived parameters, only m and n are substantially different from previous values (see Table 3.4). These reflect the influence of the acid catalyst on the reaction, and would appear to indicate that the hydrolysis of cellulose and the decomposition of glucose are less dependent on glucose concentration than has been previously found (within the range of acid concentrations used). It was in fact found during the

runs that going from 1 to 1.5% acid did not increase the glucose yields appreciably, which was one of the reaons for not carrying out experiments with higher acid concentrations.

5.3.3 Discussion

This set of experiments showed that high yields of glucose could be obtained from the hydrolysis of newsprint: conversions of cellulose to glucose of 70% and more were obtained when using 1.0 and 1.5% acid at temperatures of 230°C and higher. These yields are higher than the yields obtained by Thompson and Grethlein (1979) for newsprint hydrolysis, but high yields of glucose from newsprint hydrolysis (about 40%) have also been obtained by Church and Wooldridge (1981) at only 216°C and about 2 min residence time. But they also found that the decomposition of glucose was very dependent on acid concentration: their value of n, 1.80, is the highest of all values previously determined (see Table 3.4). It was thought that there might be some chemical in the newsprint inhibiting the decomposition of glucose under the reaction conditions employed, but methods of analysis were not available to analyse the hydrolysates completely, and find out what other reactions were taking place, and what other chemicals were present in the final product.

5.4 Refuse Hydrolysis Tests

5.4.1 Experimental programme and results

The experimental work with refuse was conducted on a sample of air-classified lights from the Doncaster RDF plant, obtained from the Warren Spring Laboratory. The sample was milled directly, as it was obtained in a preshredded form. It had been previously dried, to 15% moisture, so that it would keep better during storage. The size analysis of the sample after milling is shown in Appendix 6.

Initial problems of blockaging were experienced when trying to pump this milled refuse sample through the reactor, on account of the extraneous material in the sample, mostly plastic, which passed through

Table 5.4

Summary of refuse hydrolysis results

run no	con fig no	acid conc %	temperatures A	B	C	D	E	F	cell conv %
93	1	1.5	170	205	226	223	---	---	50.6
94	1	1.0	170	200	219	218	---	---	37.1
96	3	1.5	187	211	219	219	217	---	54.8
95	3	1.0	175	207	221	222	219	---	49.6
97a	5	1.5	190	214	217	217	217	215	49.9
97b	5	1.0	195	209	209	209	209	207	40.3
93	1	1.5	173	211	230	227	---	---	56.2
94	1	1.0	186	212	227	227	---	---	55.3
96	3	1.5	199	216	226	226	226	---	60.0
95	3	1.0	197	219	228	229	228	---	62.0
97a	5	1.5	202	226	226	226	227	227	61.4
97b	5	1.0	190	216	216	216	216	216	45.8
93	1	1.5	175	215	233	230	---	---	60.8
94	1	1.0	188	217	234	234	---	---	67.7
96	3	1.5	199	228	231	232	232	---	62.4
95	3	1.0	198	225	232	233	232	---	67.2
97a	5	1.5	217	230	230	230	230	230	62.3
97b	5	1.0	200	223	223	223	224	224	56.5
97b	5	1.0	206	228	228	227	228	228	59.7

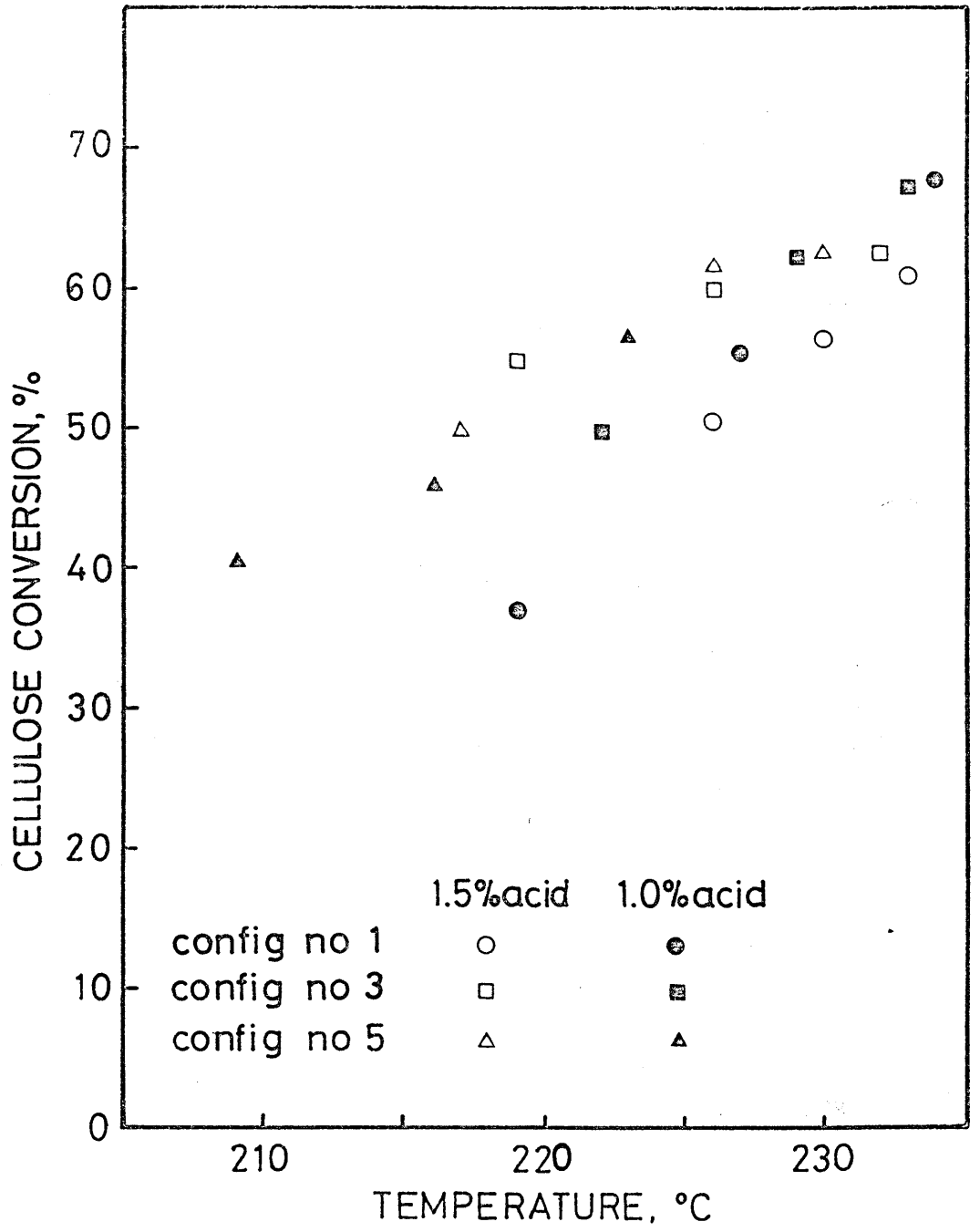


Figure 5.3. Variation of glucose yield with temperature, acid concentration and residence time (configuration number) for refuse hydrolysis.

the rig unaltered and plugged the orifice. In the end, a solution to this problem was found in replacing the orifice by a length of fine tubing, of 0.7 mm i.d., which created the back-pressure required but still allowed unreacted solids to pass through.

Five runs were then carried out, at two different acid concentrations (1.0 and 1.5%) and three different residence time configurations of the rig (Configuration Nos 1, 3 and 5). The temperature was varied between 209° and 234°C. The maximum slurry concentration used was 0.2%. Experiments were not performed with 0.5% sulphuric acid, as the results of the filter paper and newsprint work had shown that glucose yields were lower at this acid concentration.

The detailed results of these runs are listed in Table A.3.3 in Appendix 3. A total of 19 data points were obtained. These results are also summarised in Table 5.4 and plotted in Figure 5.3. Glucose yield may be seen to increase with increasing temperature, but no clear relationship between yield and acid concentration was evident. At the higher temperatures (over 230°C) higher yields were obtained using 1.0% acid than 1.5%. The highest yield obtained was 67.7%, using Configuration No 1 (total residence time 18.5 sec) and 1% acid, with a maximum temperature of 234°C. Several other data points were obtained where the cellulose conversion to glucose was over 60%; these were with Configuration Nos 3 and 5, at temperatures of 225°C and above.

5.4.2 Estimation of kinetic parameters

The same method of estimating kinetic parameters was used as for newsprint (see section 5.3.2 above). The same temperature correction was made for the data points for which the initial temperature (A) at the end of the preheating section was above 180°C. After allowing for an initial glucose content C_{B0} of 0.1 (i.e. assuming an amorphous cellulose content C_{A0} of 0.9) the kinetic parameters derived by Saeman (1945), Fagan et al (1971) and Thompson and Grethlein (1979) still did not fit the data; but the parameters determined above for newsprint, however, were found to fit the data very well, and by modifying several of the parameters slightly, a set of predicted values was obtained for which the sum of the deviations

was -0.007 and the sum of the squares of the deviations 0.055. The values of the kinetic parameters used in the model were:

$P_1 = 1.17 \times 10^{19}$ min^{-1}

$m = 0.50$

$E_1 = 41\,980$ cal/mol

$P_2 = 3.64$ min^{-1}

$n = 0.00$

$E_2 = 33\,130$ cal/mol

and the comparison between the predicted and actual values is shown below, in Table 5.5. As may be seen, the model predicts equally well at high and low conversions.

5.4.3 Discussion

The work with the refuse sample showed that air-classified lights may indeed be subjected to acid hydrolysis in a continuous reactor with high yields of glucose (50 to 70%) being obtained repeatedly at temperatures of 220° to 235°C. The only problems experienced were to do with the size of the rig: such problems as blockaging would not occur (or would be minimised) in a larger scale plant.

On examining the kinetics of the hydrolysis of refuse, close agreement was found with the model previously derived for newsprint. This is not altogether unexpected, as the paper fraction of refuse contains a significant proportion of used newspapers. Experiments were carried out at only two acid concentrations (1.0 and 1.5%) as the previous work with filter paper and newsprint had indicated that higher yields of glucose were obtainable at the higher acid concentrations.

Table 5.5

Refuse hydrolysis - residuals for the glucose yield model

data point	C_B(est)	C_B(real)	residual
1	0.312	0.371	0.05896
2	0.445	0.553	0.10810
3	0.605	0.677	0.07221
4	0.519	0.496	-0.02317
5	0.643	0.620	-0.02265
6	0.652	0.672	0.01998
7	0.454	0.506	0.05178
8	0.549	0.562	0.01322
9	0.631	0.608	-0.02293
10	0.541	0.548	0.00704
11	0.667	0.600	-0.06711
12	0.664	0.624	-0.03967
13	0.583	0.499	-0.08399
14	0.645	0.614	-0.03089
15	0.537	0.623	0.08570
16	0.388	0.403	0.01524
17	0.518	0.453	-0.06000
18	0.629	0.565	-0.06430
19	0.621	0.597	-0.02413
SUM OF RESIDUALS			-0.00662
SUM OF SQUARES OF RESIDUALS			0.05524

5.5.1 Experimental programme and results

A series of experiments was also carried out to investigate the decomposition of glucose at high temperature. Three runs were carried out at three different configurations of the rig (Nos 1, 3 and 5): during the course of each run, the acid concentration was altered twice, in each case after a set of samples had been taken at a range of temperatures; so in effect the decomposition reaction was investigated at three different acid concentrations for each of three different residence time variations.

As with the hydrolysis tests, the acid concentrations used were 0.5, 1.0 and 1.5%, while the temperature was varied between 187° and 237°C. The glucose feed was made up in the slurry feed tank by dissolving a measured quantity of anhydrous glucose into a measured volume of distilled water: the actual concentration was later checked by analysing a sample of feed for glucose content. In two of the runs, the initial concentration was approximately 0.3% glucose (300mg/dl), in the third 0.4%. Product samples were taken in the usual way, and analysed for glucose content (the procedure was similar to that outlined for the hydrolysate samples, in Appendix 4.2).

The detailed results of these runs are listed in Table A.3.4 in Appendix 3. A total of 39 different data points were obtained. The layout of Table A.3.4 is similar to that of Table A.3.1 for filter paper (described above in section 5.2.1) except that instead of slurry concentration, the original glucose concentration in the feed is reported, and the reaction product is analysed for glucose only. All samples were "cumulative" samples.

The results of these runs are also set out in an abbreviated form in Table 5.6. All the data points are listed, in groups of increasing temperature. Within each group, the results are further subdivided, in order of increasing residence time (Configuration No) and decreasing acid concentration. The decomposition of glucose may be seen to increase with both acid concentration and temperature: but at each temperature level,

Table 5.6

Summary of glucose decomposition results

run no	con fig no	acid conc %	temperatures A	B	C	D	E	F	gluc conv %
85a	1	1.5	182	187	182	180	---	---	12.6
83a	3	1.5	191	193	187	179	172	---	14.5
84b	5	1.5	186	189	187	179	175	171	14.8
85a	1	1.5	189	206	201	199	---	---	21.9
85b	1	1.0	187	202	199	198	---	---	18.1
85c	1	0.5	191	202	199	198	---	---	16.3
83a	3	1.5	197	207	210	193	186	---	25.3
83b	3	1.0	197	206	202	196	190	---	27.7
83c	3	0.5	195	202	198	192	187	---	17.3
84b	5	1.5	189	203	199	189	183	178	22.3
84c	5	1.0	190	197	195	185	181	177	14.3
84a	5	0.5	188	206	201	190	185	180	12.4
85a	1	1.5	195	223	220	219	---	---	49.7
85b	1	1.0	193	223	220	219	---	---	39.2
85c	1	0.5	189	218	215	213	---	---	27.6
83a	3	1.5	198	220	217	210	203	---	46.3
83b	3	1.0	201	221	221	211	205	---	46.1
83c	3	0.5	194	220	216	208	202	---	32.6
84b	5	1.5	192	217	215	210	204	198	40.1
84c	5	1.0	198	216	216	214	208	202	34.9
84a	5	0.5	189	215	214	206	201	194	21.5
85a	1	1.5	200	226	230	230	---	---	59.6
85b	1	1.0	199	226	228	228	---	---	50.8
85c	1	0.5	199	223	226	227	---	---	41.8
83a	3	1.5	206	224	229	226	218	---	63.4
83b	3	1.0	209	227	226	223	216	---	54.3
83c	3	0.5	200	226	226	224	216	---	45.8
84b	5	1.5	206	227	227	227	226	223	61.7
84c	5	1.0	204	226	225	225	225	222	53.5
84a	5	0.5	197	225	226	226	226	223	44.2
85a	1	1.5	207	230	237	237	---	---	71.2
85b	1	1.0	205	228	234	235	---	---	59.8
85c	1	0.5	203	224	234	235	---	---	52.0
83a	3	1.5	215	228	237	236	235	---	74.0
83b	3	1.0	217	232	235	234	233	---	67.6
83c	3	0.5	213	232	235	234	234	---	61.1
84b	5	1.5	213	235	235	235	235	235	69.6
84c	5	1.0	213	234	233	233	233	233	68.1
84a	5	0.5	206	233	233	233	233	233	61.1

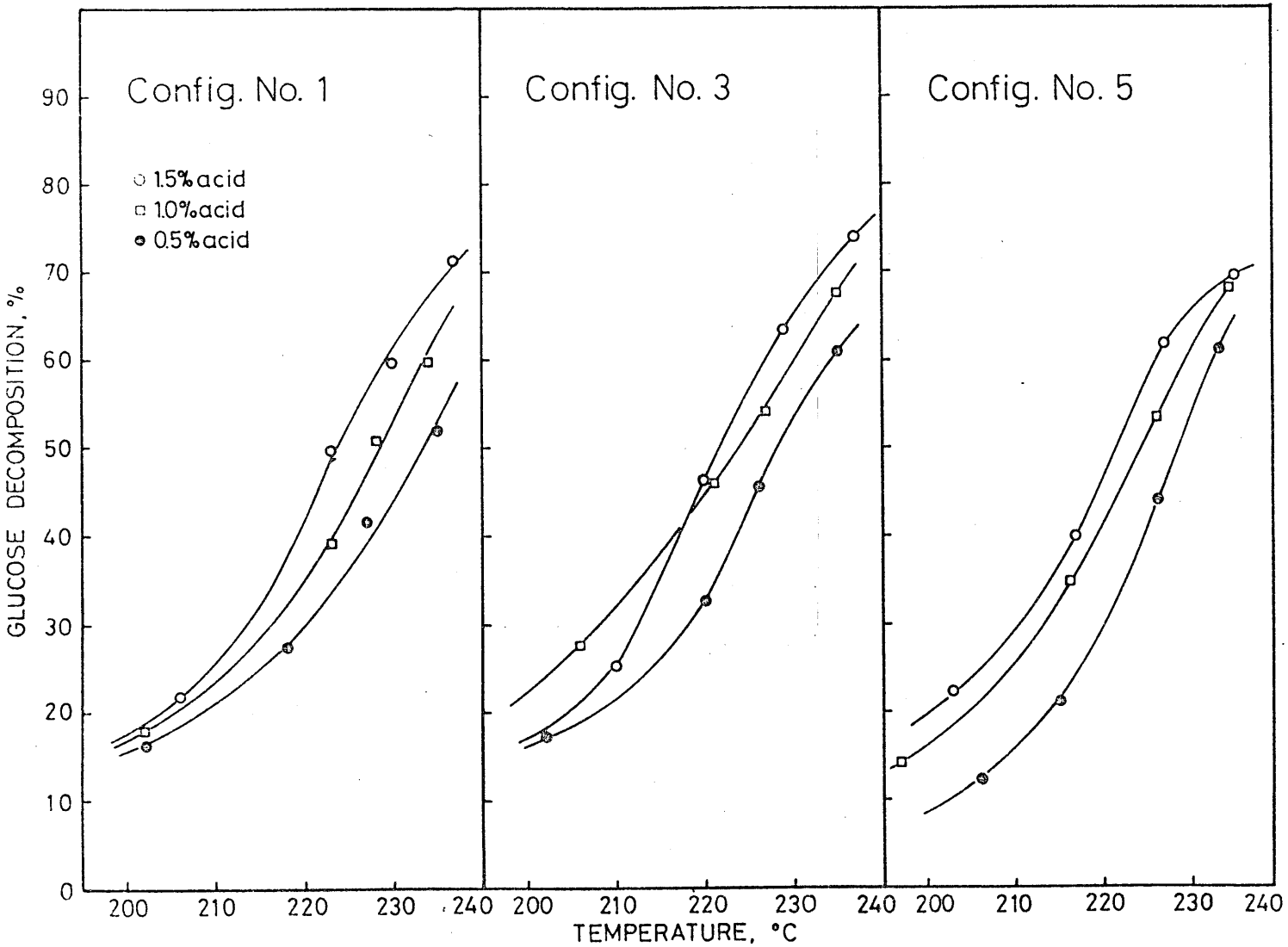


Figure 5.4, Extent of glucose decomposition at various temperatures, acid concentrations and residence times (configuration numbers).

the decomposition appeared to reach a maximum at Configuration No 3. These results are also plotted, in Figure 5.4.

5.5.2 Estimation of kinetic parameters

A numerical integration method similar to that employed for the cellulosic substrates was used to estimate kinetic parameters to describe the results of the glucose decomposition tests. It was assumed that the reaction was first-order, and that equation 5.3 could be used to describe the value of the rate constant as a function of temperature and acid concentration. Values of P_2, n and E_2 were sought that most accurately predicted the experimentally determined values.

Reaction was once again assumed to start only at 180°C, and in those instances where the temperature at the reactor inlet was higher than 180°C, an extra heating stage was added to the calculations, in which the temperature rose from 180°C to whatever the temperature was at the end of the preheating section (point A). As before, the temperature was assumed to vary linearly between points in the rig where the temperature was measured.

The kinetic parameters which fitted the data best were those of Thompson and Grethlein (1979), but the fit was actually not very good. A better correlation was obtained by modifying the parameters slightly, to give

$$P_2 = 3.59 \times 10^{14} \text{ min}^{-1}$$

$$n = 0.59$$

$$E_2 = 32\,150 \text{ cal/mol}$$

but even with these values the sum of the deviations between predicted and actual values was -0.426 and the sum of the squared deviations 0.509.

It is known that glucose undergoes other acid-catalysed reactions besides decomposition at elevated temperatures, such as dehydration and reversion (polymerisation) and the kinetic model of a first-order reaction is probably too simplistic to represent the sequence of reactions accurately. The model is nevertheless useful in that it allows the prediction of glucose yields from the hydrolysis of cellulosic materials.

The significant extent of decomposition at high temperatures (over 70% at 237°C using 1.5% acid) adds weight to the hypothesis that some inhibitory effect was taking place during the hydrolysis of newsprint and refuse which resulted in the high yields that were obtained.

5.6 Limitations of the Present Work and Recommendations for Future Work

5.6.1 Particle size

Because of the small scale of the rig, and the very real possibility of blocking the orifice, the experimental work had necessarily to be limited to feedstocks of very small particle size. Before the hydrolysis experiments. therefore, all the cellulosic materials investigated (filter paper, newsprint, refuse) were knife-milled to a particle size finer than 200 microns. Other investigators working with small-scale apparatus in the field of acid hydrolysis of cellulosic materials have had the same problem, too. Thompson and Grethlein (1979), in their studies with a continuous reactor, used Solka-Floc which had been ball-milled to a particle size finer than 74 microns, and newsprint of particle size finer than 200 microns.

As discussed in sections 3.6 and 3.7, however, fine grinding or particle size reduction is one of the most effective pretreatment methods for enhancing cellulose hydrolysis, by increasing the availability or accessibility of cellulose for reaction. The kinetics of the hydrolysis of finely ground cellulose is thus likely to be different from that of larger particles. And as grinding is an energy-intensive operation, it is unlikely that it will ever be used commercially as a pretreatment method for cellulose hydrolysis.

The rig therefore needs to be scaled up to allow work to be done on the hydrolysis of larger particles. Recent work by Guha et al (1978), who compared the rate of hydrolysis of 2.5 mm prehydrolysed wood chips with that of sawdust, showed that diffusional effects were indeed significant with the larger particles. And in the original work of Saeman (1945) with Douglas fir cellulose, evidence was obtained that the rate of hydrolysis

becomes slower with particle sizes greater than 20 mesh (>0.8 mm). An upper limit of 0.8 mm was also reported by Church and Wooldridge (1981) in their investigations of the hydrolysis of newsprint in a continuous reactor.

Inasmuch as newsprint (and paper in general) is a form of cellulose which has already been subjected to a certain degree of pretreatment in the papermaking process, it follows that less drastic methods are required (than with native cellulose) to bring it to a form in which the cellulose is readily available for reaction. Shredding followed by soaking in water for a number of hours, or a mild prehydrolysis at 100°C (during which some of the products of hemicellulose hydrolysis could be recovered) might well be sufficient to allow rapid high-temperature hydrolysis to proceed. The hydrolysis reaction itself, of course, also has the effect of breaking down the particle size: Figures 5.5 to 5.7 show photographs taken with the scan electron microscope of the ground cellulosic feedstock used in the present experimental work. The fibrous nature of both filter paper and newsprint may clearly be seen, and the high proportion of extraneous (non-cellulosic) material in the newsprint is also evident. Figure 5.8 shows a photograph of the solid residue remaining after one of the newsprint hydrolysis experiments: here it may be seen how the fibrous structure has been broken down, and the average particle size is very much smaller than in the original sample.

Experiments using feedstocks of larger particle size, generated by different methods of pretreatment than intensive knife milling, ought to be one of the first priorities of any further experimental work, conducted with larger equipment. It might well be, however, now that the orifice has been replaced by a length of fine tubing of larger diameter (than the orifice), that these tests could be conducted using the present rig as it stands, or by replacing the fine tubing by a longer length of slightly larger diameter.

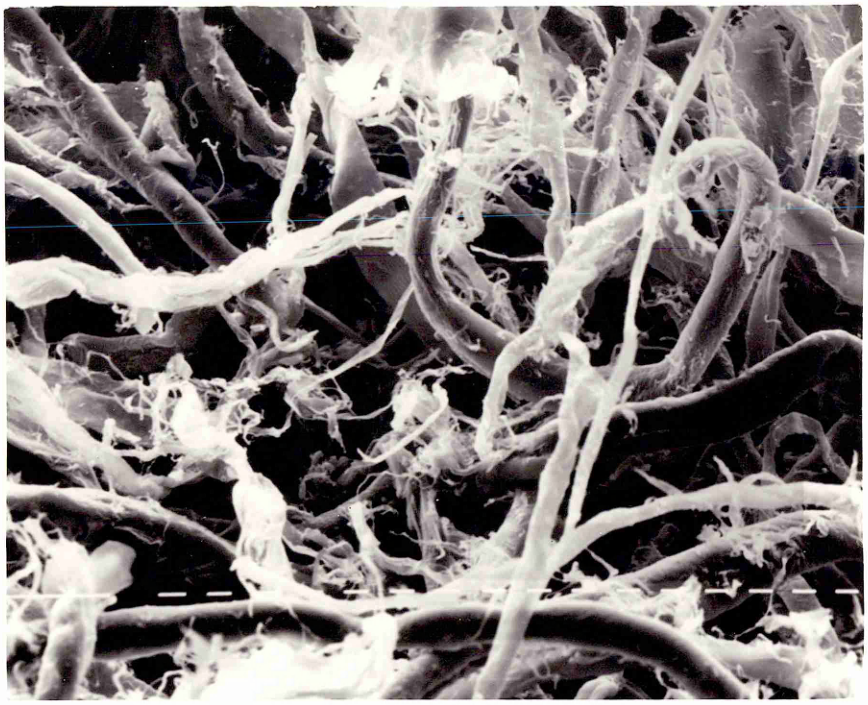


Figure 5.5 SEM photograph of ground filter paper feedstock (magnification 320 times)

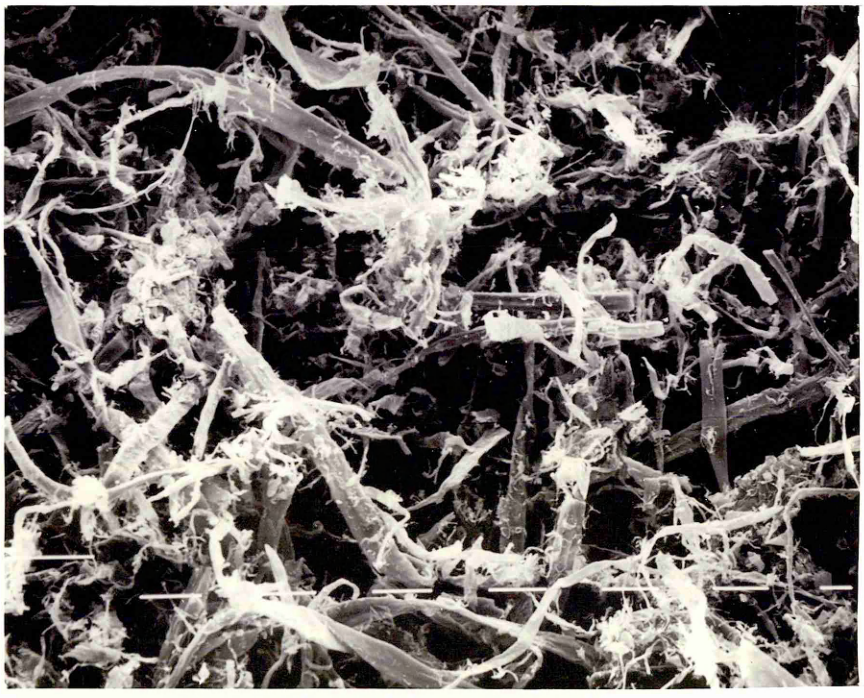


Figure 5.6. SEM photograph of ground newsprint feedstock (magnification 80 times)

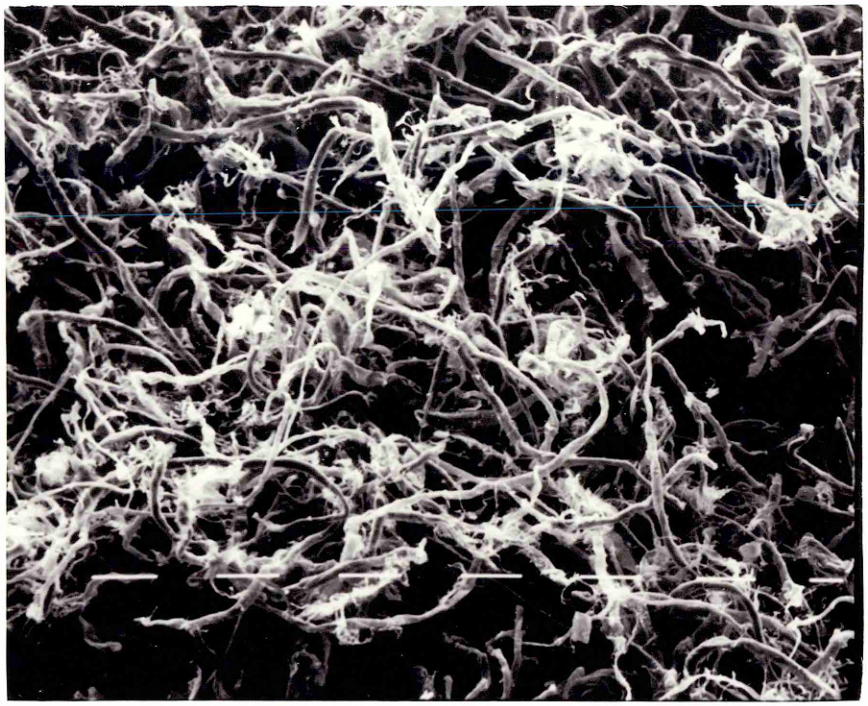


Figure 5.7. SEM photograph of ground filter paper feedstock (magnification 80 times)

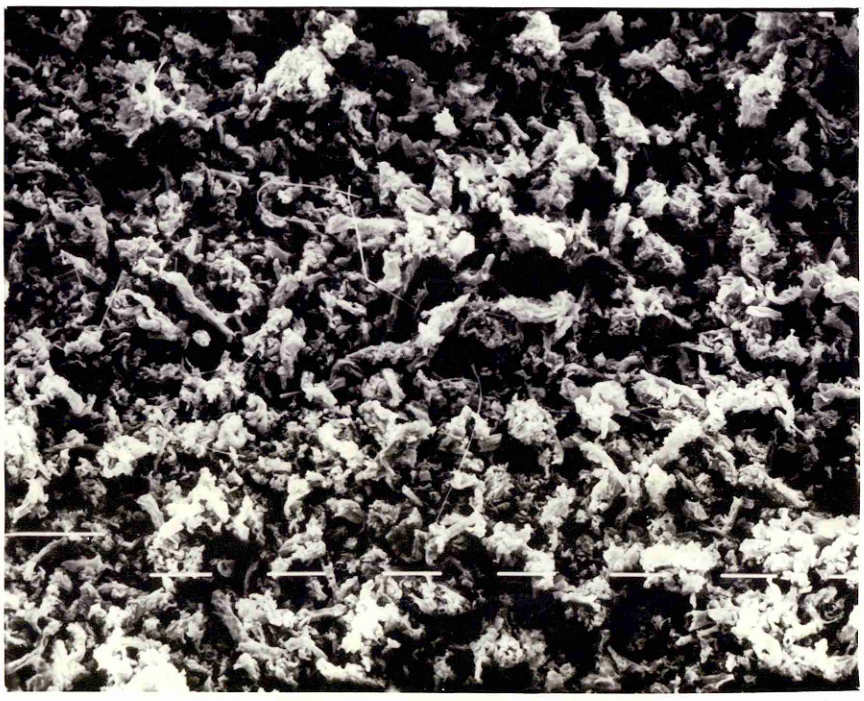


Figure 5.8. Solid residue from newsprint hydrolysis (magnification 80 times)

5.6.2 Slurry concentration

Another problem arising from the small scale of the experimental equipment was that slurry concentrations were limited to less than 0.3% solids. This limitation might also be overcome now that the orifice has been replaced by a length of fine tubing. In a commercial application, it is important for a hydrolysis reactor to be able to treat a feed with a high solid/liquid ratio so as to obtain a high concentration of sugar in the hydrolysate. If the hydrolysate has first to be concentrated from 0.1 or 0.2% glucose to 10% prior to fermentation, the additional evaporation costs could well be prohibitive.

The low slurry concentrations employed in the present experiments also limited the work in a number of other respects. Difficulties with the analytical procedure have already been discussed (section 4.3.3): the low concentrations of glucose in the hydrolysate meant that samples had to be concentrated 10 to 20 times by rotary vacuum evaporation prior to analysis by HPLC. Other products of hydrolysis, such as hydroxymethylfurfural and levulinic acid, as well as the products of hemicellulose hydrolysis, should be present in smaller concentrations still, which would make quantitative analysis even more difficult. In this project, only glucose determinations were carried out, but it would be interesting, especially from the viewpoint of a commercial application, to investigate the kinetics of the production of other products, too, from newsprint and air classified lights. Using higher slurry concentrations in the feed to the reactor would make analysis for these products much easier.

Finally, because of the low slurry concentrations employed, even the analyses for glucose were carried out at the lower end of the Industrial Analyser's range. The instrument measures up to 2000 mg/dl of glucose, but almost all the hydrolysate readings were between 0 and 200 mg/dl. Any errors in analysis would thus be made more serious because of the low concentrations involved.

Future work with a larger-scale rig, therefore, or perhaps to a limited extent with the present rig, should investigate the hydrolysis of more concentrated slurries of newsprint or air classified lights, to determine

whether the kinetics of hydrolysis are affected by the increase in solids concentration and to study the rate of formation of byproducts of the process.

5.6.3 Temperature profile

It may be shown that in consecutive first-order reactions, where the selectivity (ratio of k_1 to k_2) increases with temperature, the highest yield of intermediate product is obtained when operating isothermally at the highest temperature practicable. For cellulose hydrolysis, this means that the slurry should be heated instantaneously to the desired operating temperature, and held at that temperature for the optimum residence time (after which the reaction should be quenched instantly). Ideally, instantaneous heating would be carried out by the injection of live steam, but this was not available at the University. Instead, the heating of the slurry was made as rapid as possible by the use of small diameter tubing and high wattage heating cords.

If the work is to be continued in a larger-scale rig, it would be worthwhile locating the plant in the vicinity of a small package boiler which could deliver steam at 240°C. Modifying the rig so that heating can be accomplished by live steam injection would allow higher theoretical yields to be achieved, and would also simplify the calculations when determining the kinetic parameters.

Thompson and Grethlein (1979) solved the problem of carrying out an isothermal reaction by adding acid catalyst only after the slurry had been preheated to the desired reaction temperature. When doing it this way, the problem is to ensure instantaneous and good mixing of the acid with the preheated slurry; it is also difficult to set the acid concentration precisely, even with the aid of metering pumps.

5.6.4 Materials of construction

Because of the highly corrosive nature of sulphuric acid at high temperature, the rig had to be made of corrosion-resistant material. All the tubing and compression fittings used were made of 316S stainless steel, which is the most easily obtainable material which can be used for

this application. There are other alloys which have superior acid-resistant qualities, but tubing made of these materials would have had to have been made to order, which could have resulted in long delays. The original rig, made of the larger diameter tubing (1 in o.d.), needed welded flanges because of the high operating pressures - the welding, which had to be done outside the University, took six months to complete! (This was another reason for wanting to use smaller diameter tubing, as then compression fittings could be used quite adequately at the high pressures.)

In the event, the 316S stainless steel tubing stood up well to the reaction conditions. There were four accasions when one of the final heating coils had to be replaced because of acid corrosion right through the tube, but in every case it appeared that the corrosion had been in a weak spot in the material, usually no bigger than a pinprick, as the tubing on either side of the hole did not show appreciable signs of corrosion. The effects of corrosion were perhaps most marked in the fixed orifice, which had to be replaced every 5 or 6 runs as the hole would become too large to maintain the required back-pressure in the system. This phenomenon would have been compounded, however, by the effect of erosion, as the hydrolysate passed through the orifice at very high velocities.

The effects of acid corrosion were also very obvious on the thermocouple probes, which were not made of 316S stainless steel. The sheath material was made of type 321 stainless steel, which has poorer acid-resistant qualities than 316S. Initially, the thermocouple probes were bent into an "L" shape when inserted into the slurry flow, but it was soon found that after three or four runs the sheath would crack along the bend. Figure 5.9 shows one such thermocouple probe, whose sheath was split open, exposing the elements which form the hot junction. By the time this thermocouple was replaced, the extent of corrosion had become very severe: Figures 5.11 and 5.12 are photographs taken with the aid of the scan electron microscope, which show how the metal of the thermocouple wire and sheath material respectively was eaten away, leaving grain boundaries of metal more resistant to acid attack. Figure 5.10 is a detail of the fixed orifice, showing how the head of the nut was eaten away by the action of the sulphuric acid at high temperatures.

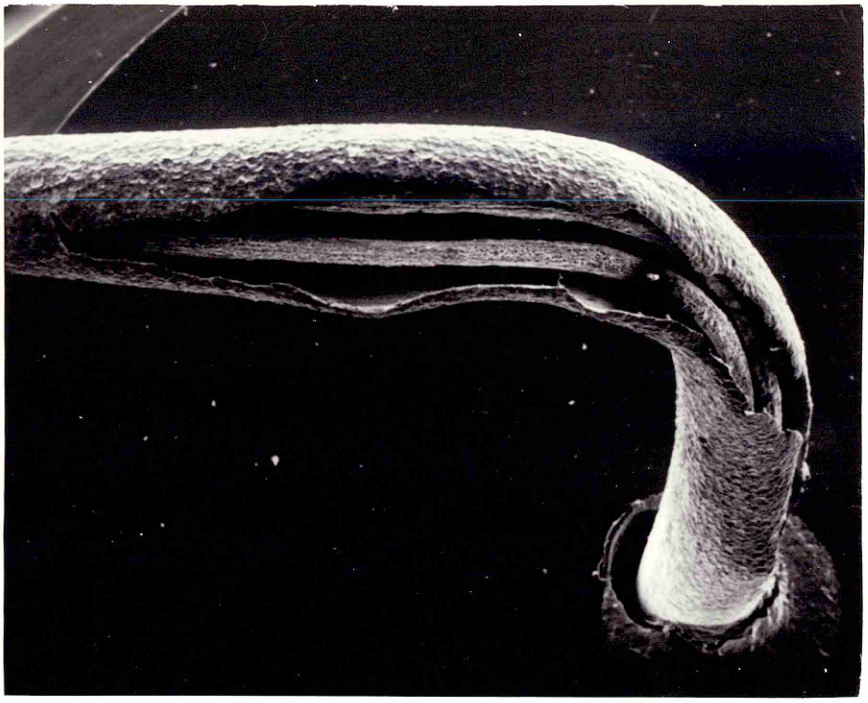


Figure 5.9. Surface of thermocouple probe showing corrosion (magnification 20 times)

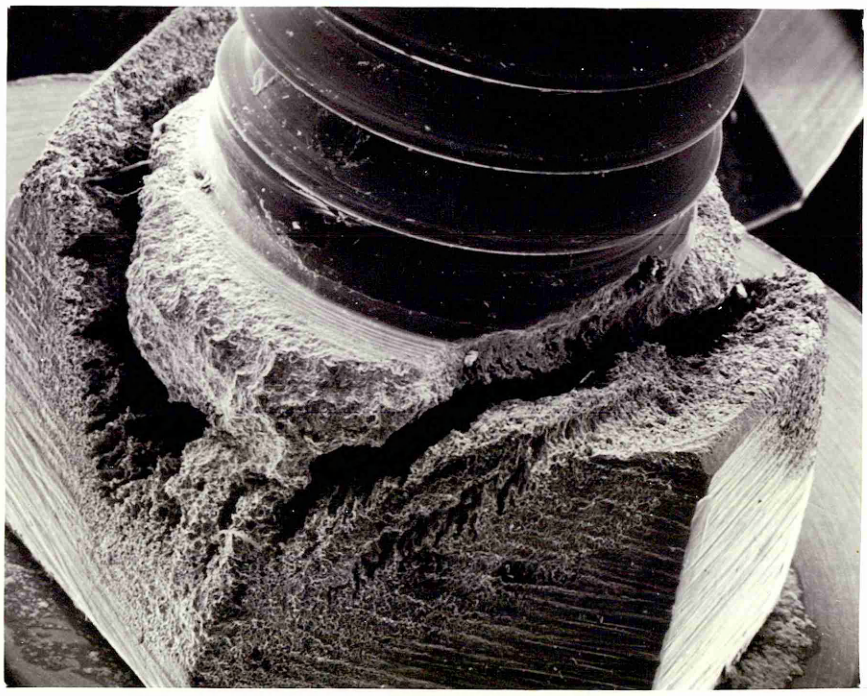


Figure 5.10. Acid corrosion of fixed orifice (magnification 20 times)

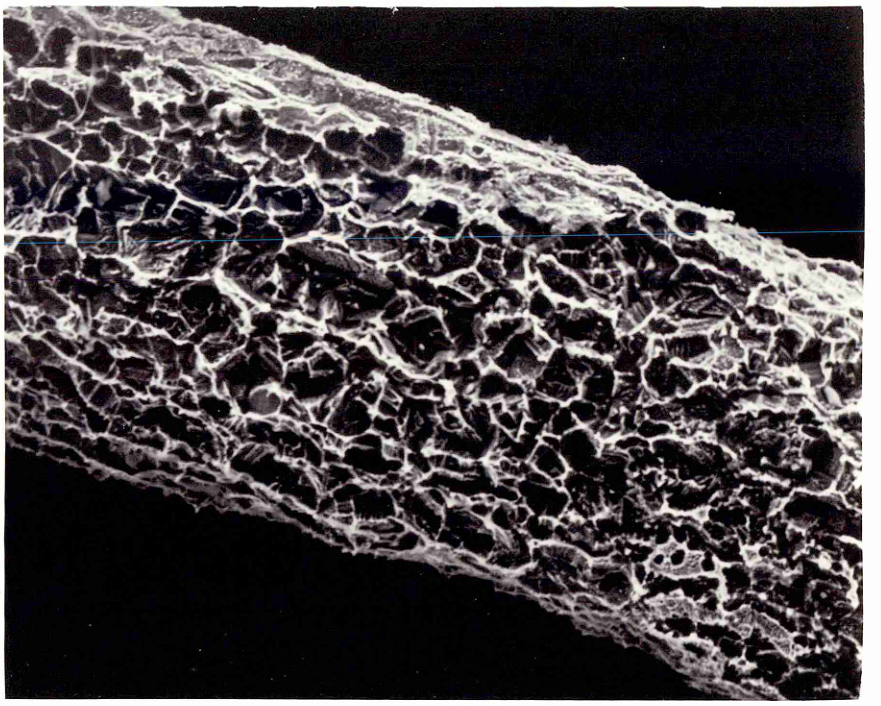


Figure 5.11. Detail showing corrosion of thermocouple element (magnification 320 times)

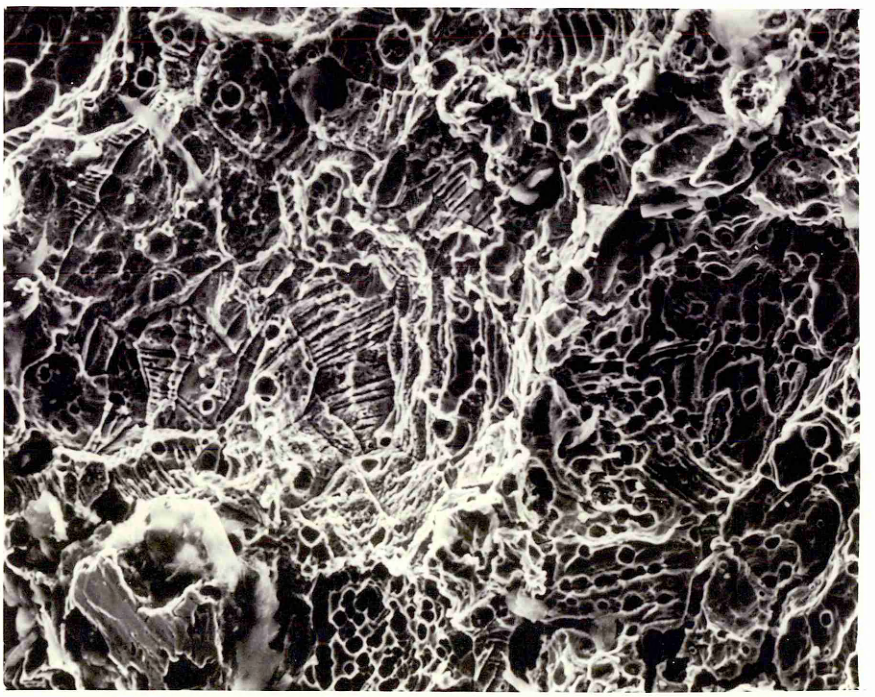


Figure 5.12. Detail showing corrosion of thermocouple sheath (magnification 320 times)

In order to save the thermocouple probes from having to be replaced too often, a type of thermowell arrangement was devised (see Figure 4.13) wherein the probes were encased in an outer sheath of very small wall thickness, made of fine 316S stainless steel tubing. This outer sheath bore the brunt of the acid corrosion, and could be replaced easily and inexpensively when it no longer afforded protection to the thermocouple probe.

In future work with a larger scale rig, the possibility ought to be investigated of constructing those parts of the rig where the slurry is at high temperature (ie the reactor section) of material which is more resistant to acid corrosion, such as Monel or Carpenter 20-Cb3. It might also be possible to have tubing lined with PTFE, which is impervious to mineral acids: the only point to bear in mind with this is that the upper limit of the working temperature of PTFE is about 230° to 240°C.

5.6.5 Axial dispersion

In all the calculations, to estimate the kinetic parameters and predict glucose yields, it was implicitly assumed that the flow in the reactor could be considered as plug-flow. This was rather difficult to verify in practice, as ideally the axial dispersion of the slurry needed to be measured, but to pass slurry through the rig without carrying out a hydrolysis reaction inevitably resulted in the orifice blocking. To gain an idea of the flow characteristics, however, an axial dispersion test was made by pumping water through the system and switching to a dilute glucose solution in a "step input". Samples of the effluent stream were taken at 15 sec intervals, and analysed for glucose. A plot of the glucose concentration versus time is shown in Figure 5.13.

As may be seen, after breaking through, the glucose concentration reached its final value after 60 sec, after which it remained constant. The concentration reached 85% of its final value after 30 sec. This is a rather crude measure of the axial dispersion in the reactor, as it includes the dispersion in the heating coils, and (more significantly) in the flexible rubber hosing connecting the valves at the outlet of the feed tanks to the suction port of the pump. It does, however, set an upper

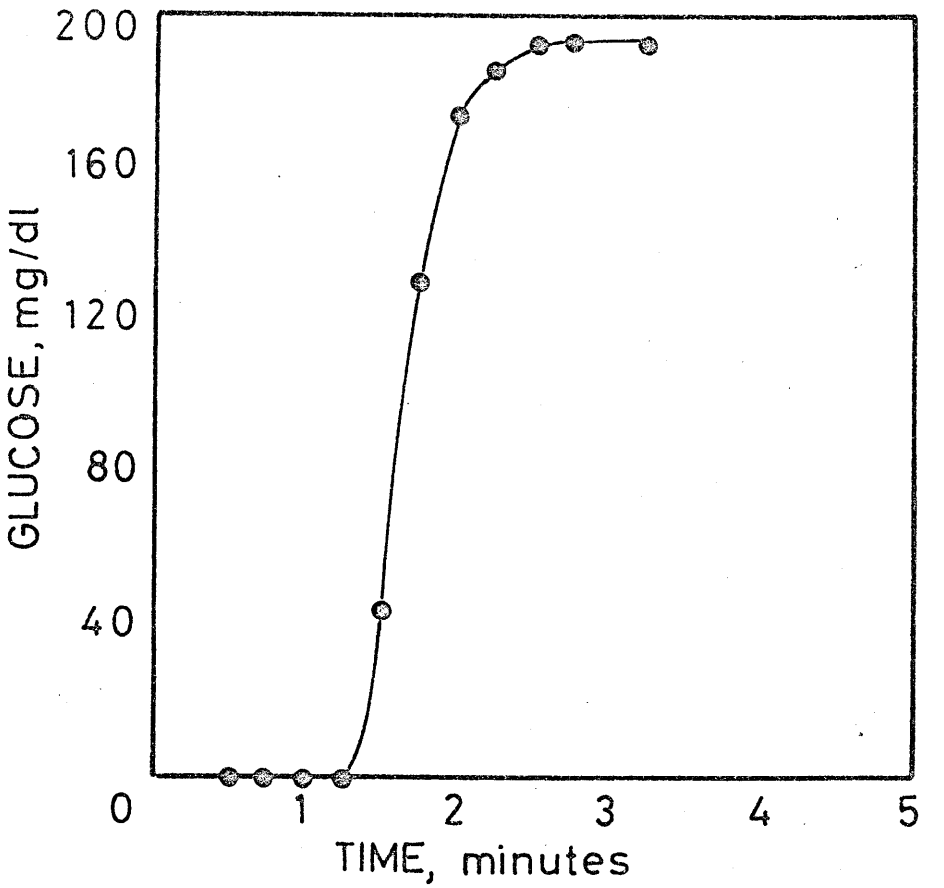


Figure 5.13. Axial dispersion in modified rig - plot of glucose vs residence time.

limit on the extent of dispersion taking place within the system.

A better indication of the axial dispersion in the reactor would be obtained by injecting an inert tracer into the slurry at the end of the preheating section during a run, and monitoring the concentration of tracer in the effluent. In the absence of such an experiment, it was assumed that a significant part of the dispersion occured in the stages of the rig prior to the reactor section. In future work, the dispersion could be kept at a minimum by hard plumbing the feed lines, and keeping the condenser section as short as possible.

5.7 Summary and Conclusions

The experimental results presented in this chapter show that the continuous reactor developed by modifying the original rig could be used successfully to carry out the acid hydrolysis of cellulosic materials under controlled conditions, and to obtain rate data from which kinetic parameters could be evaluated. Although reaction was non-isothermal, rapid heating and accurate temperature measurement and control resulted in high yields of glucose and made it possible to use a numerical integration method to estimate the kinetic parameters.

In the initial experiments, filter paper (which is pure cellulose) was used as a model substrate. Runs were carried out at three different acid concentrations (0.5, 1.0 and 1.5%) at temperatures varying from 205° to 240°C and at 5 different residence time configurations of the rig. Glucose yield was found to increase with increasing acid concentration, temperature and residence time in the reactor, and to go through a maximum as the residence time was increased for the same temperature and acid concentration. The highest yield obtained was 47.7%, when using 1.5% sulphuric acid at a maximum temperature of 233°C and a total residence time of 20.4 sec. The kinetic parameters obtained agreed well with the previously published values of Thompson and Grethlein (1979), which may be said to have been corroborated by this work.

Hydrolysis tests using newsprint and refuse as cellulosic feedstocks were carried out at approximately the same range of temperatures but at

only three different residence time configurations of the rig. In the newsprint runs, the acid concentration was varied from 0.5 to 1.5%: with refuse, tests were conducted with 1.0 and 1.5% H_2SO_4 only. High yields of glucose were obtained, reaching 74.3% for newsprint (1% acid, 231°C, 38 sec residence time) and 67.7% for refuse (1% acid, 234°C, 18.5 sec residence time). Previously published kinetic parameters were found not to fit either set of results, so new values were sought which would fit the model and keep within the previously determined ranges. The parameters found to fit the newsprint data were also found to fit the refuse results. In both cases, C_{A0}, the original crystalline cellulose content of the feedstock, was taken as 0.9, and C_{B0}, the fraction of cellulose originally in an easily hydrolysable form, as 0.1. Problems were experienced when trying to pump the milled refuse sample through the rig, on account of extraneous material, mostly plastic, passing through the system unaltered and blocking the orifice, but these were overcome by replacing the orifice with a length of fine tubing of small diameter, which allowed the inert solids to pass through while still creating sufficient back-pressure.

An investigation of the decomposition of glucose at elevated temperatures was also carried out at acid concentrations varying from 0.5 to 1.5% and three different residence time configurations, at temperatures varying from 187° to 237°C. Decomposition was found to increase with increasing acid concentration and temperature, but appeared to go through a maximum with increasing residence time. The extent of decomposition was considerable at the higher temperatures, reaching over 70% at 237°C when using 1.5% acid. The kinetic parameters found to describe the results did not match those found previously, indicating that reactions other than decomposition are taking place.

Overall, the success of this work lies in the development of the reactor to the point where hydrolysis experiments could be carried out with repeatable results and under known and controlled conditions; in the corroboration of the kinetic parameters of Thompson and Grethlein (1979) through an extensive investigation of the hydrolysis of filter paper; and in carrying out the hydrolysis of typical cellulosic wastes, namely, newsprint and refuse. In particular, the hydrolysis of the air-classified light fraction of municipal refuse was shown to be technically feasible.

Yields of glucose in excess of 60% of the available cellulose were obtained repeatedly at temperatures of 220° to 235°C, and the results were in good agreement with predictions made using the best kinetic parameters found for newsprint.

The limitations of the work were largely a result of the small scale of operation. Problems of blockaging meant that the cellulosic feedstocks had to be reduced to a very small particle size, and that slurry concentrations were limited to less than 0.3% solids. Although heating by means of electrical heating cords was rapid, instantaneous heating by live steam injection would have been preferred, but this was not available at the University. It is recommended that future work be carried out with a larger-scale rig, of small pilot plant size (capable of treating, say, 40 to 50 kg/hr of solids) to investigate the hydrolysis of slurries of higher solid/liquid ratios and larger particle size.

This rig should ideally be located at the Warren Spring Laboratory or in a university Chemical Engineering Department which has the back-up facilities to support work of this kind - such as a boiler plant which can supply steam at 250°C, and an analytical laboratory where determinations for other products in the hydrolysates (besides glucose) could be made. Work should also be done on improving the materials of construction, especially in the reactor section which is at high temperature, to minimise the effects of acid corrosion.

CHAPTER 6

PROCESS DESIGN AND ECONOMIC ANALYSIS

6.1 Introduction

A secondary aim of this work was to use the kinetic information obtained from the hydrolysis experiments with refuse to draw up a preliminary design of a process plant for this application, and an order-of-magnitude cost estimate. This is done in the present chapter. The design which is presented is based on utilising the cellulosic part of municipal solid waste, although a comparison is also made of the cost and profitability of using source-separated paper (newsprint) as a cellulosic feedstock.

A hydrolysis process designed to treat cellulose in refuse may have a capacity of several hundred tonnes depending on its location - in section 2.2.1 seven metropolitan areas were identified in which the total waste arising is of the order of 7 million tonnes annually, or 38% of the total waste collected in England and Wales. These are the areas where the problem of disposal is greatest, and where a plant of this kind would be a practical proposition. The distance over which the waste would have to be transported would also not be too great, and in many cases sites would already exist (in the form of bulk transfer stations or, as at Doncaster and Byker, refuse derived fuel plants) which could possibly be extended to accomodate a hydrolysis plant.

A design capacity was chosen of 500 tonnes per day of sorted air-classified lights with a moisture content of 20% and a nominal cellulosic content of 40%. It was assumed that this material would be obtained from a multi-resource recovery plant treating municipal solid waste of the type shown in Figure 2.1. The aim of the design was to produce ethanol from this material by hydrolysis and fermentation in place of the RDF pellets

which are currently produced, and to evaluate the cost of the plant and the potential for profitability of the process, compared with the present waste disposal methods.

The plant design uses a 10% pulp slurry in an isothermal plug-flow reactor. A number of simplifying assumptions have been made to facilitate the mass balance calculations, namely

(1) that no reactions occur other than the hydrolysis of cellulose, but that the non-cellulosic organics enter the liquid phase;

(2) that the weight of the decomposition products equals the weight of the cellulose hydrolysed;

(3) that the decomposition products are in the liquid phase, and are precipitated out in the neutraliser, together with the non-cellulosic organics;

(4) that the kinetic parameters determined for the hydrolysis of refuse will hold good at a slurry concentration of 10%.

6.2 Choice of Reaction Conditions

The choice of reaction conditions will ultimately be an economic decision, of balancing marginal glucose yield against the cost of operating at higher reaction temperatures and increased acid concentrations. Higher temperatures also correspond to shorter residence times, and it eventually becomes impractical to increase the temperature any more, because of the difficulty in carrying out a controlled reaction.

Table 6.1 shows values of the maximum yield of glucose obtainable from the hydrolysis of cellulose in refuse under isothermal conditions, and the corresponding residence times, t_{opt}, for temperatures between 215° and 235°C and acid concentrations of 1.0 and 1.5%. These values were calculated using the parameter values for k_1 and k_2 determined from the experiments with air-classified lights, substituted into the equations (Grethlein, 1978):

$$C_B(max) = C_{AO} (K/A^K)^{1/(1-K)} \quad \text{..... equation 6.1}$$

where

$$A = 1 + (C_{BO}/C_{AO})(k_1 - k_2)/k_1 \quad \text{..... equation 6.2}$$

and $K = (k_1/k_2)$

and

$$t_{opt} = \{1/(k_1 - k_2)\} \ln(K/A) \quad \text{..... equation 6.3}$$

Values of C_{AO} and C_{BO} were taken as 0.9 and 0.1 respectively (see section 5.3.2).

Table 6.1

Maximum glucose yield and optimum isothermal reaction time for acid hydrolysis of refuse

	C_B(max), %		t_{opt}, sec	
temp °C	1.0% acid	1.5% acid	1.0% acid	1.5% acid
215	0.600	0.619	52.5	47.3
220	0.617	0.647	35.2	31.4
225	0.635	0.669	23.7	21.0
230	0.655	0.688	16.1	14.2
235	0.673	0.705	11.0	9.7

As expected, the maximum glucose yield increases with increasing temperature and acid concentration, with corresponding decrease in optimum reaction time. On examining the figures, there would appear to be little to be gained from operating at the higher acid concentration: the marginal yield of glucose is small, for the cost of using 50% more acid. At the same time, increasing the temperature by 20°C from 215 to 235°C results in an improvement in cellulose conversion from 0.600 to 0.673, but the reaction time drops from a very manageable 52.5 sec to a mere 11 sec.

It was decided, therefore, for the purposes of this design, to select a temperature of 220°C, and an acid concentration of 1.0% for the reaction

conditions; and a corresponding reaction time of 35.2 sec. The residual cellulose concentration at t_{opt} is found by using equation 3.8: $C_A = 0.167$. By difference, C_C, the concentration of decomposition products, is 0.216.

6.3 Plant Description

Air-classified lights from a municipal waste sorting process are transferred from a storage hopper by conveyor belt to a blender, which has a turbine agitator. Process water which has been preheated to 80°C is added to make up a slurry of approximately 12.5% solids, and 75°C. The slurry is pumped through a preheater, to raise the temperature further to 120°C before being pumped into the reactor.

At the reactor inlet, the slurry is brought up to the reaction temperature by the continuous addition of live saturated steam. Enough 50% acid is also injected to give a 1% acid concentration in the slurry. With the condensation of the steam, and the acid injection, the solids content in the slurry is now 10%. The hydrolysis occurs as the slurry passes through the reactor. The extent of cellulose conversion will depend on the heat-up time of the slurry, the completeness of acid mixing, the residence time distribution, and the degree of temperature control - but for the purposes of this preliminary design, the value derived from the kinetic model above will be taken as being a reasonable estimate of glucose yield.

The reaction is quenched by flash evaporation of the hydrolysate as it leaves the reactor and enters a flash tank, which is maintained at 134°C and 310 kPa (30 psig). The liquid removed from the flash tank is pumped to a neutraliser where a 33% lime slurry is added continuously to a CSTR with 15 min residence time. The neutralisation is carried out while the hydrolysate is still hot as the solubility of calcium sulphate is minimised (its solubility decreases with increasing temperature). The decomposition products arising from the hydrolysis reaction and the non-cellulosic organics originally present in the feed are assumed to be precipitated out as well, as the pH is raised.

From the neutraliser, the hydrolysate passes to a continuous centrifuge, where the solids (lignin, unreacted cellulose, calcium sulphate, decomposition products and non-cellulosic organics) are separated out. The final solids content in the centrifuge cake is taken to be 33%: this cake is dried and burned in a boiler to raise part of the heating requirements of the process.

The liquid leaving the centrifuge is still hot (134°C) and is used to preheat the feed before that stream enters the reactor. The dilute glucose solution, now at 85°C, enters the evaporators, where it is concentrated from about 4% glucose to 10%, which has been found to be optimum for economic fermentation (Cysewski et al, 1976). A triple effect evaporator unit is used, with steam to the first effect being provided by the flash vapour from the flash tank. Batch fermentation follows, resulting in an alcohol solution of approximately 6% by volume. This is distilled to 99.5% v/v ethanol in the distillation plant, and pumped to the final product tank.

No allowance is made for the recovery of any byproducts. A flowsheet of the plant appears in Figure 6.1.

6.4 Plant Sizing and Equipment Costing

In this section, the major items of equipment are individually sized and costed. From this, an estimate is made of the fixed capital cost of the whole plant, using the Lang factor method (Holland et al, 1974). Most of the equipment costs were obtained from Peters and Timmerhaus (1980), Bridgwater and Mumford (1979) and Hall et al (1982), and were brought to a common basis of January 1982 prices using the PE plant cost index. As the "location index" of Britain with respect to the United States is 0.96 (Williams, 1980) cost estimates from the American sources were first converted to the sterling equivalents using the appropriate value of the foreign exchange rate (published monthly by HMSO in "Financial Statistics").

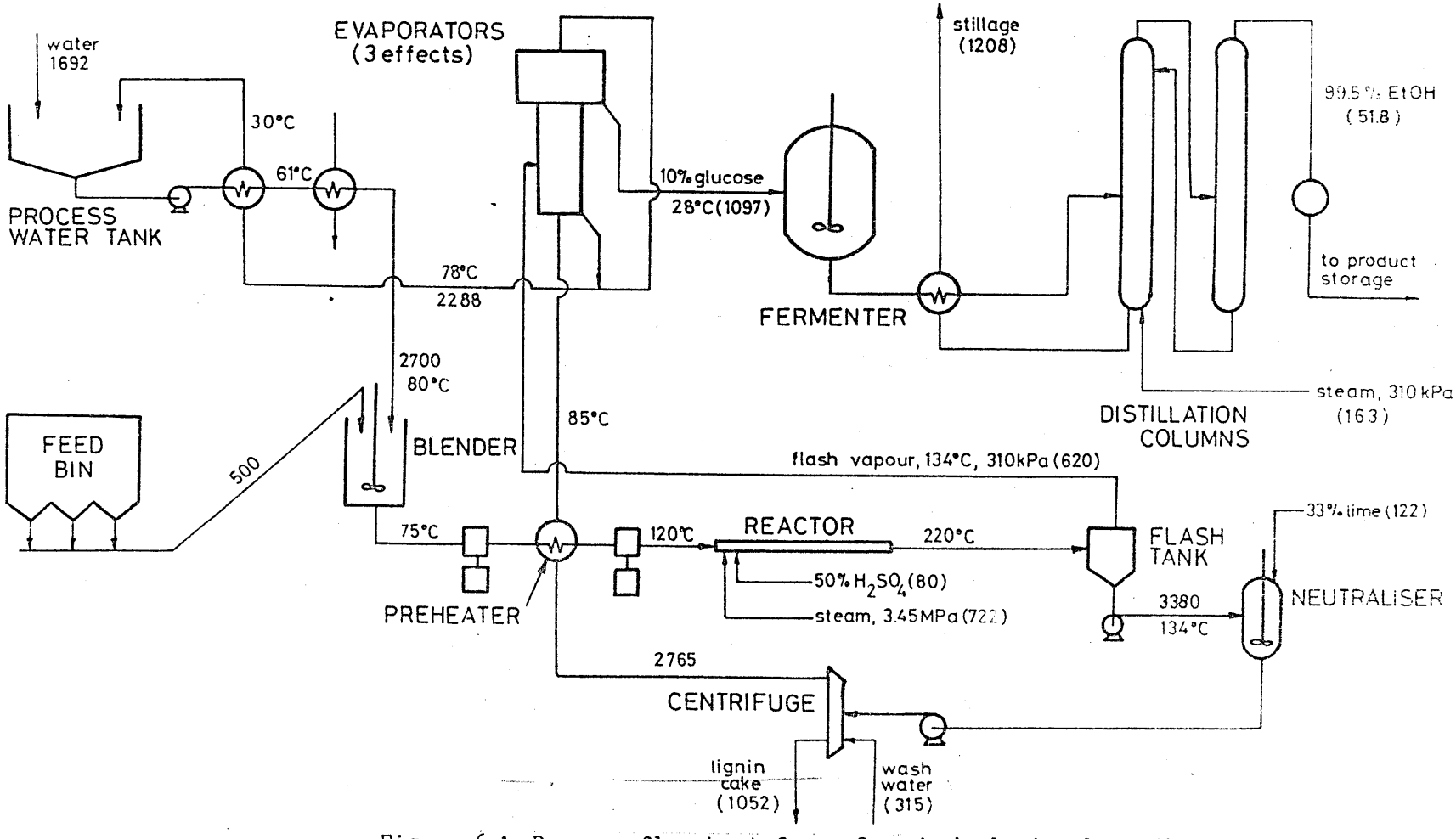


Figure 6.1. Process flowsheet for refuse hydrolysis plant. Material flow in (tonne/day).

6.4.1 Feed storage bin

Storage capacity for 3 days is required, ie 1500 tonnes, in order to level out fluctuations in supply and allow continuous plant operation. Assuming an average density for air classified lights of 300 kg/m^3 gives a bin design volume of 5000 m^3. The estimated cost at Jan 1978 prices is £50 000 (Bridgwater and Mumford, 1979): correcting for the PE index gives an estimated cost for Jan 1982 of £75 000.

6.4.2 Belt conveyor

A 30 m long belt conveyor is specified, of belt width 0.76 m (30 in). The estimated cost in the U.S. at 1979 prices is $30 000 (Peters and Timmerhaus, 1980). The estimated cost in Britain for Jan 1982 is £20 000.

6.4.3 Slurry blender

The slurry blender mixes 500 tonnes per day of shredded waste with 2700 tonnes per day of process water. The capacity is calculated on the basis of a residence time of 15 min. Thus, 28m^3 of blender capacity is required. Three slurry blenders of 10m^3 each are specified. The material of construction is Type 304 stainless steel. The U.S. cost including agitator and drive is $12 000 each at Jan 1982 prices (Hall et al, 1982). The total cost in Britain for Jan 1982 is taken to be £18 000.

6.4.4 Reactor

The flow reactor dimensions are a function of the required residence time, the throughput and the desired flow velocity. The residence time has already been set (section 6.2) at 35.2 seconds. The throughput is obtained from a mass and energy balance calculation around the reactor.

Reactor inputs:

500 tonne/day solids (20% moisture), 120°C

x tonne/day make-up water, 120°C

y tonne/day H_2SO_4 (50%), 20°C

z tonne/day saturated steam, 3.45 MPa

The final desired slurry concentration is 10% solids. The required acid concentration in the reactor is 1%. The desired reaction temperature is 220°C. The slurry feed has been preheated to 120°C, while the acid has not been preheated. The specific heats of 50% H_2SO_4 (= 0.60cal/gm°C) and wood (=0.55cal/gm°C) were obtained from Perry (1963), as were the data for water. A mass and enthalpy balance over the final slurry (after steam condensation) gives

x = 2700 tonne/day
y = 80 tonne/day
z = 722 tonne/day

Thus the slurry at the reactor inlet will contain 40 tonne/day H_2SO_4 (100%), 400 tonne/day air-classified lights (dry basis) and 3560 tonne/day of water. From the densities of these materials, also obtained from Perry (1963), the overall density of the slurry at the reactor inlet may be found: 0.79 tonne/m^3. The volumetric flow rate of slurry through the reactor is thus 5048 m^3/day, and as the desired residence time in the reactor is 35.2 sec, the required volume is 2.06 m^3. The reactor will be made of 316S stainless steel 12 in Schedule 40 pipe, the required length being 28.5 m. This will be provided by four units, each 7.1 m (24.3 ft) in length. The cost of a carbon steel pipe of this diameter in Britain in April 1976 was £143.2/m (Capital Cost Estimating, 1979). The present cost of the entire reactor made of stainless steel pipe at Jan 1982 prices is estimated to be £35 000.

6.4.5 Flash tank

Before the required volume of the flash tank can be calculated, it is necessary to know the composition of the reaction products (hydrolysate). Another mass balance must be made, this time over the reactor outlet, taking into account the chemical reaction which has occurred. This is largely dependent on the nature of the feed which is assumed to contain

40% cellulose
20% non-cellulosic organics
40% inerts

According to the kinetic analysis made above (section 6.2) at the desired

reaction conditions, the fractional conversion of cellulose to glucose is 0.617; the fraction of cellulose remaining unreacted is 0.167; and the fraction of cellulose converted to decomposition products is 0.216. The inerts will still be in the solid phase at the end of the reactor, while the non-cellulosic organics are all assumed to enter the liquid phase, but not to undergo reaction. The material leaving the reactor will thus contain:

glucose (in solution): 109.7 tonne/day

organics (in solution): 80 tonne/day

decomposition products (in solution): 34.6 tonne/day

sulphuric acid (in solution): 40 tonne/day

water : 3549 tonne/day

(water consumed during hydrolysis = 11 tonne/day)

cellulose (unreacted) : 26.7 tonne/day

The material and enthalpy balance around the flash tank may now be calculated. The hydrolysate, which is at 220°C, is flashed to 134°C and 310 kPa. If F is the mass of water entering the flash tank, and V and H are the vapour and liquid phases leaving the flash tank respectively, the overall mass balance is:

$$F = V+L \quad \text{..... equation 6.4}$$

The enthalpy balance is

$$FH_F = VH_V + LH_L \quad \text{..... equation 6.5}$$

By definition,the fractional vapourization e is

$$e = V/F \quad \text{..... equation 6.6}$$

Solving equations 6.4 to 6.6 simultaneously gives

$$e = (H_F-H_L)/(H_V-H_L) \quad \text{..... equation 6.7}$$

From the known values of H_F, H_L and H_V, the value of e may be found to be 0.175. Thus 17.5% or 620 tonne/day of the entering water is vapourized leaving 2929 tonne/day of water still in the liquid phase. The flash chamber is designed for a vapour residence time of 30 seconds. The vapour density of steam at 400 K and 100 kPa is 0.5542kg/m^3 (Wong,1977). The required volume of the flash tank is thus 125m^3. The estimated cost of a vessel this size made of 316 SS, is £30 000 at Jan 1977 prices (Bridgwater and Mumford, 1979). The estimated cost at Jan 1982 prices is £49 000.

6.4.6 Neutraliser

The neutraliser is a CSTR with a residence time of 15 min. A lime slurry is added containing sufficient lime to neutralize 40 tonne/day of sulphuric acid, ie 40.8 tonne/day $CaCO_3$. The slurry is made up to 33% solids, so the water content is 81.6 tonne/day. The total input to the neutraliser is 3315.7 tonne/day, so the volume required (allowing for 70% filling) is 50m^3. The cost of such a vessel in the U.S. is estimated at $62 000 at Jan 1982 prices (Hall et al,1982), so the estimated purchase cost in Britain at the same time is £35 000.

6.4.7 Centrifuge

After neutralization the glucose decomposition products, as well as the non-cellulosic organics are assumed to be in the solid phase in addition to the unreacted solids from the reactor and the calcium sulphate formed. The quantity of solid to be removed is 357 tonne/day, which is in a slurry with 3146 tonne/day of liquid. The centrifuge cake is washed with water of a quantity equal to 10% of the incoming liquid, to recover any glucose in the solids. The solid cake is assumed to have an eventual solids content of 33%.

Three 36 in helical conveyor centrifuges are specified, of 316 SS, which are estimated to cost $125 000 each in the U.S. at Jan 1982 prices (Hall et al, 1982). The estimated cost in Britain is £65 000 each, or a total of $200 000.

6.4.8 Preheater

The clarified solution coming out of the centrifuge is used to heat the feed slurry to the reactor from 75° to 120°C, before entering the evaporators. The heat load in the preheater is thus

$$q = \{ (mC_p)_{solids} + (mC_p)_{water} \} \times (T_2 - T_1) \quad \text{..... equation 6.8}$$

$$= \{ (400 \times 10^3 \times 2.3) + (2800 \times 10^3 \times 4.216) \} \times (120 - 75)$$

$$= 5.7 \times 10^8 \text{ kJ/day}$$

The final temperature of the hydrolysate is calculated to be 85°C (using $C_p = 4.2$ kJ/kg°C). A counterflow heat exchanger is used, and the overall heat transfer coefficient is taken as 454 W/m^{2}K (Peters and Timmerhaus, 1980). The required exchanger area is 1227 m^2. Three exchangers are specified, of 410 m^2 each. The estimated cost is £15 000 each, at March 1976 prices (Capital Cost Estimating, 1979); the cost at Jan 1982 is put at £85 000.

6.4.9 Evaporators

A triple effect evaporator unit is specified to concentrate the sugar prior to fermentation. The liquid entering the evaporators has a glucose content of 4%, while batch fermentation requires an initial sugar concentration of about 10%.

It was assumed in the calculations that the boiling point elevation due to the solute content is negligible, and that the heat transfer coefficients for the first, second and third effects are 3123, 1988 and 1420 W/m^{2}K (550, 350 and 250 Btu/(ft^2)(hr)(°F)) respectively. The specific heat of the solution was taken as 4.184 kJ/kg°C. The steam to the first effect is the vapour from the flash tank, 620 tonne/day at 134°C and 310 kPa. Because the feed temperature is reasonably high, a forward feed arrangement of the evaporators is used.

From the usual material and enthalpy balances around the evaporators, by trial and error procedure, the required surface area of each evaporator was found to be 196 m^2. The vapour temperatures in the three effects are 110°, 81° and 28°C. The total steam requirement is 588 tonne/day; the steam available as flash vapour from the flash tank is 620 tonne/day, so no additional steam is required. The total condensate is 2288 tonne/day, with an average temperature of 78°C: this is used to preheat the process water before it is made into a slurry with the solid feed.

The cost of the evaporators (vertical tube) is estimated at $200 000 each at Jan 1979 prices (Peters and Timmerhaus, 1980). The cost in the U.K. at Jan 1982 prices is estimated at £400 000.

6.4.10 Fermenters

The flow rate to the fermenters is 1097 tonne/day or about 1100 m^3/day, containing 109.7 tonne/day of glucose. The fermentation is a batch process, requiring 20 hr of fermentation time, so a total holdup time of 24 hr is specified, to allow for cleaning and sterilising the fermenters between batches.

The fermenters are designed for a liquid loading of 80% of maximum capacity, ie a total of 1375 m^3 is required. This will be provided by four vessels of 350 m^3 each. The total cost at Jan 1982 prices is estimated at £80 000 (Paul, 1980).

6.4.11 Distillation

The yield of ethanol by fermentation of glucose is a theoretical 51.1%, but the maximum normally produced is 47%, or 51.5 tonne/day of ethanol. This is produced as an approximately 6% v/v solution in the fermenters, and proceeds to the distillation plant, where it is distilled to 99.5% ethanol (65.5 m^3). Distillation is carried out in a stripper/rectifying column and a dehydration tower, with stillage removed from the bottom of the stripping column being used to preheat the cool beer arriving from the fermenters. The heat for distillation is provided by saturated steam at 310 kPa. The cost of the entire distillation plant was obtained using a scale factor method (sf = 0.7) from a detailed plant design and economic avaluation by R. Katzen Associates (1980) of a process producing ethanol from corn. The estimated purchase cost for the whole plant, at U.K. prices in Jan 1982, is estimated to be £200 000.

6.4.12 Product storage tank

The product storage tanks are designed to hold one week's production, ie 460 m^3. This is provided by four tanks, of 120 m^3 each. The estimated cost, at Jan 1982 prices, is $25 000 each (Hall et al, 1982). The comparable cost in the U.K. is estimated at a total of £50 000.

6.4.13 Acid storage tank

This is also designed to hold one week's requirements, or 153 m^3 of concentrated acid. The cost of such a tank in the U.S. in Jan 1979 is estimated to be $30 000 (Peters and Timmerhaus, 1980): the U.K. cost in Jan 1982 is set at £21 000.

6.4.14 Process water tank

This is designed to hold sufficient water to provide one day's make-up requirements, ie 1692 m^3/day. A tank of this size is estimated to cost $70 000 at Jan 1979 prices (Peters and Timmerhaus, 1980); or, in Britain, in Jan 1982, £50 000.

6.4.15 Process water preheater

Condensate from the evaporator section at 78°C is used to preheat the process water before it is made into a slurry with the solid feed in the blenders. The final temperature of the condensate is taken to be 30°C: it may be calculated that the temperature of 2700 tonne/day of process water is raised from 20° to 61°C. A counterflow heat exchanger is specified, of 140 m^2. The estimated cost at March 1976 prices is £6000 (Capital Cost Estimating, 1979). The cost at Jan 1982 prices is estimated to be £12 000.

6.4.16 Process water booster heater

The process water is heated further to 80°C before it enters the blenders. Heating is accomplished with saturated steam at 310 kPa. The amount of steam required is 99 tonne/day. The heat exchange area needed is 14 m^2, costing an estimated £2600 in March 1976 (Capital Cost Estimating, 1979); or, for Jan 1982 prices, £5000.

6.4.17 Waste disposal plant

About 1200 m^3 of stillage are produced daily, which require disposal. The cost of a plant to treat this effluent is estimated at £150 000 (Bridgwater and Mumford, 1979) at Jan 1982 prices.

6.4.18 Package boiler

Process steam for the plant is provided by a package boiler, which will be fired on coal and will also burn the dried lignin cake from the centrifuges. The total steam requirements are 722 tonne/day at 3.45 MPa and 262 tonne/day at 310 kPa: a total of 25.2 MW. The estimated cost of a package boiler is obtained from Peters and Timmerhaus (1980), of $400 000 in Jan 1979. Brought to Jan 1982 prices in Britain, this item of equipment is estimated to cost £280 000.

6.4.19 Pumps

The estimated purchase costs of the pumps required in the plant are listed in Table 6.2. All pumps have been specified in duplicate, so as not to hold up production in case of a fault. All cost estimates were obtained from Peters and Timmerhaus (1980).

6.4.20 Total plant cost

A list of the major items of equipment and their estimated purchase cost appears in Table 6.3. The total cost is multiplied by a Lang factor of 3.63 (Holland et al, 1974) to arrive at an estimated installed cost, which includes the cost of piping, insulation, land, buildings, services, and contractor's fee. To this must be added the installed cost of the waste disposal plant and the package boiler. Allowing for a contingency of 20%, the estimated fixed capital cost of the entire plant, at Jan 1982 prices, is £8.1 million.

6.5 Operating Costs

The estimated operating costs of the plant are summarised in Table 6.4. The plant is assumed to operate for 330 days per year. The cost to the municipality of the raw material is taken as £8 per tonne, which is the estimated selling price of air classified lights. Refuse derived fuel pellets normally sell for about £10 per tonne (Temple-Pediani, 1981), but the drying step which ususally precedes pelletisation would be omitted if the material was hydrolysed instead. The price of bulk chemicals was

Table 6.2

Estimated cost of process pumps

application	type	capacity l/min	number reqd	total est. cost Jan 1982 (£)
slurry pump	recip.	900	6	150 000
reactor pump	recip.	675	8	190 000
flash liquid pump	centrif.	1350	4	16 000
acid pump	recip.	91	2	13 200
lime pump	centrif.	91	2	1320
neutraliser pump	centrif.	2500	2	4000
evaporator pump	centrif.	900	2	1320
fermenter pump	centrif.	900	2	1320
alcohol product pump	centrif.	55	2	660
process water pump	centrif.	1125	4	5000
stillage pump	centrif	900	2	1320
TOTAL				384 140

source: Peters and Timmerhaus, 1980.

Table 6.3

Estimated capital cost for 500 tonne/day refuse hydrolysis plant

item	purchase cost, Jan 1982 (£)
Process water tank, 2.25 Ml	50 000
Process water preheater, 150 m^2	12 000
Process water booster heater, 15 m^2	5 000
Feed bin, 5000 m^3	75 000
Belt conveyor	20 000
Blender, 10 m^3 (x3)	18 000
Slurry preheater, 410 m^2 (x3)	85 000
Reactor, 0.32 m diam x 7.1 m length (x4)	35 000
Acid storage tank, 150 m^3	21 000
Flash tank, 125 m^3	49 000
Neutraliser, 50 m^3	35 000
Lime storage tank, 150 m^3	21 000
Centrifuge, 0.9 m diam helical conveyor (x3)	200 000
Evaporators, 3 effects, long vertical tube, total area 600 m^2	400 000
Fermenters, 350 m^3 (x4)	80 000
Distillation section	200 000
Product storage tank, 120 m^3	50 000
Pumps	384 140
Total process equipment purchase cost (A)	1 740 140
Estimated installed cost of process equipment (A x 3.63) (includes piping, insulation, structural steel, land, buildings, services, contractor's fee)	6 316 708
Waste disposal plant (installed cost)	150 000
Package boiler (installed cost)	280 000
Estimated total installed cost	6 746 708
+ 20% contingency	1 349 342
FIXED CAPITAL COST	8 096 050

Table 6.4

Annual operating cost for 330 day plant operation per year

	£ sterling, Jan 1982
raw materials	
air classified lights, 500 tonne/day at £8/tonne	1 320 000
sulphuric acid, 40 tonne/day at £35/tonne	462 000
lime, 40.8 tonne/day at £20/tonne	270 000
yeast, ammonia, oxygen for fermentation (est.)	100 000
	2 152 600
utilities	
water, 1700 m^3/day at £0.25/m^3	140 250
steam, 30 MW at £6/MWh (coal)	1 425 600
electricity, 1500 kW at £25/MWh	297 000
	1 862 850
labour	
4 shifts of 8 operators, at £8000 per year	256 00
supervisor (30% of above)	76 800
overheads (100% of direct labour)	332 800
	665 600
effluent treatment	
1200 m^3/day at £0.50/m^3	198 000
maintenance	
6% of fixed capital cost	485 763
TOTAL	5 364 763

obtained from Business Monitor (1982a) while the cost of the utilities was estimated from NIFES (1980). Four shifts of 8 operators were estimated to be required to run the plant; their avarage wage was taken as £8000 per year. An extra 30% was added for the wages of supervisors, and overheads were set at 100% of direct labour cost. Effluent treatment was assumed to cost £0.50 per m^3, while maintenance costs were estimated at 6% of fixed capital cost (Peters and Timmerhaus, 1980). The total operating costs are estimated to amount, per annum, to £5 365 000.

6.6 Economic Analysis of the Process

The plant produces 51.8 tonnes/day of 99.5% ethanol. The current selling price of ethanol, obtained from Business Monitor (1982b), is £340/tonne, making the revenue from the plant £5 812 000 per annum. The plant would therefore make an operating profit of £447 000 per year, or £2.70 per tonne of air classified lights treated. If fixed charges of 10% of fixed capital cost are assumed, the plant would operate at a deficit of £363 000, or £2.20 per tonne of air classified lights treated. The price of alcohol would then need to be $361/tonne in order for the operation to break even. It is not unlikely, however, that the price of ethanol will soon reach this level: U.K. ethanol selling prices were £237/tonne in 1979, £295/tonne in 1981 and $340/tonne in the first quarter of 1982 (Business Monitor, 1982b), so the trend is certainly upward. On the basis of the present estimates, therefore, acid hydrolysis of the cellulosic material in refuse should offer good economic prospects in the near future.

It should also be remembered that the economic analysis presented above is rather conservative. No credit has been assumed for any byproducts: besides carbon dioxide which is a coproduct of the fermentation, fuffural could be recovered from the vapour leaving the flash tank, and burning the lignin residue would result in some savings on boiler fuel. The cellulose content of the air classified lights, assumed at the start of the calculations to be 40%, is also a conservative figure. The sample from the Doncaster plant which was used in the experimental work was found to have a cellulosic content of 44.4% (see Appendix 7). If the raw material to the

process plant designed above is assumed to have a cellulosic content of 45% instead of 40%, ethanol production would be 58.3 tonne/day, and the annual revenue £6 541 000. The plant would make a profit of £367 000 even after allowing for fixed charges of 10% of fixed capital cost, or £ 2.23 per tonne of air classified lights treated.

The above process design assumes that the hydrolysis plant would be attached to an existing multi-resource recovery plant, to produce ethanol in place of refuse derived fuel pellets from air-classified lights. The profits and deficits calculated above are thus in reality marginal figures, reflecting the gains or losses to be made by varying the end product of the process. The aim of hydrolysing the cellulosic content of refuse, however, is to reduce the overall cost of disposal, and how this might be done may be appreciated from the calculations which follow. These figures are no more than an indication of the possible benefits of acid hydrolysis as an alternative refuse disposal method, for (as was pointed out in Chapter 2) conditions vary markedly from one locality to the next, and using average figures need not necessarily produce correct results.

It is assumed, however, that in a certain metropolitan area, 2000 tonne/day of refuse are collected which are normally disposed of by landfilling after shredding/pulverisation at a cost of £10/tonne. It is assumed further that in place of this method of disposal, a screening plant is built which produces an air-classified light fraction for cellulose hydrolysis, and a heavy fraction (metals, putrescibles, glass, etc) which goes to landfill.

The cost of producing the air classified lights is assumed to be £6/tonne, and the cost of disposing of the heavy fraction £4/tonne (reasonable, as the volume will have been very much reduced after the removal of the light density material). Of the original refuse, 25% (ie, 500 tonne/day) is assumed to be produced as air classified lights. Then, if the air classified lights contain 45% cellulose, and the above plant design and economics are used, the overall disposal cost will become:

(cost of producing air classified lights)
+ (cost of landfilling the heavy fraction)

+ (operating cost of hydrolysis plant)

- (revenue from alcohol sales

= (2000 x 330 x £6) + (1500 x 330 x £4) + £4 045 000 - £6 541 000

= £3 444 000 per annum.

= £5,22 per tonne of original refuse.

The net cost of refuse disposal is thus almost halved.

The other option mentioned previously in this thesis is the possibility of using source-separated newsprint for acid hydrolysis. This has a higher cellulosic content than air-classified lights, 55% instead of the assumed 40%, so the yield of ethanol will be correspondingly greater - 71,25 tonne/day of 99,5% alcohol. Small changes would be required to the process plant design (in the fermentation and distillation sections) but the extra cost would be negligible. The extra revenues from alcohol sales, however, would be considerable: a total of £7 996 000 would be realised per year. As the cost of the cellulosic feedstock would once again be zero, the annual operating cost cost of the plant would be £5 045 000, and the net profits, after allowing for fixed charges of 10% of fixed capital cost would be £3 141 000, or £19/tonne of newsprint.

If the plant has to buy newsprint on the waste paper market, then the profitability of the operation would depend on the price of the newsprint. At £10/tonne, the plant would still make a profit of £1 491 000 per annum; at £20/tonne, the selling price of alcohol would have to be £347/tonne before the plant could break even.

The economics of cellulose hydrolysis may thus be seen to be very dependent on the cellulosic content of the feedstock, and its price - but in general, the outlook for this process as an alternative method of refuse disposal would appear to be very good.

CHAPTER 7
CONCLUSION

An examination of methods of refuse disposal in Britain revealed that in metropolitan areas especially, the traditional and still the most widely-used method of landfilling is becoming increasingly difficult and expensive on account of the need to transport the waste ever-greater distances to increasingly remote landfill sites. Incineration, the only other method of municipal waste disposal used in Britain to a significant extent, was seen to be even more expensive than landfilling, because of the high cost of capital equipment.

A review was made of several alternative methods of disposal, which are aimed at recovering some of the materials contained in refuse for recycling or using all or part of the organic fraction as a source of energy. Acid hydrolysis and fermentation, which aims at converting the cellulosic content of refuse to ethanol, was seen to offer many advantages, as it produces a clean, acceptable and desirable product which may be used as a fuel or chemical feedstock, as well as the possibility of obtaining by-products and lignin, which may be used as a process fuel.

An investigation of the nature of cellulosic materials, from the point of view of hydrolysing cellulose to glucose, found that the crystallinity of the cellulose molecule, and (to a lesser extent) its close association with lignin, limit the availability of cellulose for reaction. Carrying out a dilute acid hydrolysis at elevated temperatures, however, offers the possibility of obtaining high conversions of cellulose while minimising the decomposition of the glucose product. Previous work in this field, in the last ten to fifteen years, showed that high yields of glucose could indeed be obtained under these reaction conditions; but experiments had been performed mostly with pure or relatively pure cellulosic substrates, and there was a need to extend the work to refuse, which had been shown to be the most promising substrate for cellulose hydrolysis from a commercial

standpoint. In addition, only one group of researchers had obtained kinetic data for the hydrolysis of cellulose in a continuous reactor operated at high temperatures, and these figures needed corroboration.

Accordingly, an existing rig which had been designed and constructed at the Open University for cellulose hydrolysis, but which had not previously been made to work satisfactorily, was modified so that reaction could be carried out under the controlled steady-state conditions required for obtaining rate data. Through a series of preliminary experiments, changes were made to the pressure regulatory system, the method of controlling and measuring temperature, and to the physical dimensions of the rig, to allow more rapid heating to the desired reaction temperature, and accurate temperature control. The modified rig was then operated for over 30 runs, for a total of over 17 hours, to obtain more than 170 data points describing the hydrolysis of cellulose and the decomposition of glucose at elevated temperatures under the action of dilute sulphuric acid.

The experimental parameters investigated were acid concentration, reaction temperature and reactor residence time. Acid concentrations were varied from 0,5 to 1,5%; temperature from 180° to 240°C; and residence time from 16 to 36 seconds. The substrates used were filter paper, newsprint and air classified lights of municipal refuse, as well as pure glucose. The work with filter paper gave yields of up to 47,7% of potential glucose, and kinetic parameters which agreed well with those of Thompson and Grethlein (1979). The experiments with newsprint and air classified lights gave higher yields of glucose - over 70% and more - but the results did not agree with those predicted by previous researchers, so new sets of kinetic parameters were obtained for the model. It was found that the parameters obtained for newsprint could be used quite well to predict the results of the experiments with refuse.

On the basis of the data obtained from the hydrolysis of the refuse sample, a preliminary design was drawn up of a process plant to produce ethanol from the air classified light fraction of municipal refuse. The initial capital investment was estimated to be £8,1 million for a 500 tonne/day plant. If the cellulose content of the raw material was assumed to be 45%, it was found that the municipality would be £367 000 a

year better off by opting for acid hydrolysis and fermentation instead of turning the material into RDF pellets. The marginal cost of the raw material to the municipality was taken as £8/tonne, the selling price of ethanol as £340/tonne, and fixed charges were assumed to be 10% of fixed capital cost.

A very rough estimate of a complete process to produce ethanol from untreated refuse, with the heavy fraction being disposed of by conventional landfilling, indicated that considerable savings in overall disposal costs could be made, compared with disposing of all the material by landfilling after shredding/pulverisation. Hydrolysing source-separated newsprint, which has a higher cellulose content than air classified lights, was seen to have an even greater profit potential, but the economics are very dependent on the cost of the raw material.

To follow on from this work, it is recommended that the reactor be scaled up to pilot plant size to allow the investigation to be made of the hydrolysis of slurries of higher solid/liquid ratios and larger particle sizes. It is also recommended that heating the slurry by live steam injection be carried out, if possible; that the recovery of byproducts from hydrolysates be investigated; and that materials of construction having better acid-corrosion resistant properties than 316S stainless steel be examined.

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APPENDICES

APPENDIX 1

METHODS OF ANALYSIS

A.1.1 Glucose Analysis

A.1.1.1 HPLC and differential refractometry

In the first series of preliminary runs, high performance liquid chromatography (HPLC) was used to separate and determine the glucose content in the hydrolysates. The analyses were carried out by Mr Graham Jeffs in the University's Chemistry Department, using the method of Palmer (1975a, 1975b).

A DuPont Model 830 HPLC Instrument was used, together with a DuPont Model 845 Refractive Index detector. The column used was a Lichrosorb NH_2, 22.5 cm x 5 mm i.d., at room temperature. The eluent was an 80:20 mixture of acetonitrile and water. The flow rate was 1.1 ml/min at a pressure of 3.62 MPa (525 psig). Samples of 10 to 20 microlitres were injected via a Rheodyne 7120 sample valve.

The concentration of glucose in the hydrolysate was determined from peak-height measurement, relative to a peak-height standard curve prepared using known standards, made up in the laboratory. It was found that the hydrolysate samples as received were unsuitable for direct injection, as they (a) contained large quantities of suspended solids, (b) were too acidic, at pH 1 to 3, and (c) were too dilute with respect to glucose to be detected by the refractive index detector.

All samples had thus to be prepared by noting the initial mass, adjusting the pH to 6 to 7 by adding $Ca(OH)_2$ to a constantly stirred solution, filtering to remove the calcium sulphate and all the other solid

materials, and evaporating the excess water from the sample solution in a Buchi rotary vacuum evaporator at 40°C. All samples were reduced in bulk to 10 to 20% of the original mass before analysis.

A.1.1.2 Immobilised enzyme assay

In the second series of preliminary runs, and in all the final experiments with the modified rig, glucose content was measured using a YSI Model 27 Industrial Analyser. This instrument relies on a thin layer of immobilised glucose oxidase enzyme which reacts with glucose almost instantaneously to form hydrogen peroxide: this in turn diffuses to a platinum electrode, where it is measured, yielding a measurement of the amount of glucose oxidised by enzyme action.

Samples of 25 microlitres are injected into a sample chamber by means of a Syringepet repetitive pipettor. The instrument is calibrated using standard glucose solutions of 200 and 500 mg/dl (approximately 0.2 to 0.5%) to provide a direct readout of the concentrations. The assay is completed in 60 sec, and the result displayed on a digital meter.

During the final four series of experiments, the filter paper hydrolysate samples were analysed directly without any form of pretreatment: the newsprint samples gave very high readings initially, and drifted with time. For these, and the remainder of the experiments, the hydrolysate samples were neutralised prior to glucose analysis. This was found to give steady and repeatable results.

A.1.2 Cellulose Determination

The cellulose content of the filter paper, newsprint and refuse used in the hydrolysis experiments, and of the solid residues from the newsprint hydrolysis, was determined by the quantitative saccharification method (Saeman, Bubl and Harris, 1945). This is an analytical technique in which cellulose is hydrolysed to glucose with a minimum amount of glucose decomposition.

A ground cellulosic sample of about 0.4 g is weighed into a boiling tube and mixed with 5 ml of 72% sulphuric acid that has been cooled to 15°C. The tube is placed in a water bath at 30°C for 45 min, with stirring at 5 to 10 minute intervals. After 45 minutes, the tube is removed from the water bath, and the mixture washed into a conical flask with 140 ml of distilled water. The flask is placed in an autoclave, and held there for one hour at 15 psig (120°C). After cooling, the solution is filtered, made up to 250 ml in a standard volumetric flask, and a sample taken for neutralisation and analysis for glucose. The yield is the maximum potential glucose yield for the sample,

$$\frac{\text{weight glucose}}{\text{weight sample}} \times 100$$

For pure cellulose, the potential glucose yield should be 111.1%: thus, to obtain the cellulose content of a sample, the potential glucose yield is divided by 1.11. The results obtained from the quantitative saccharification of the filter paper, newsprint and refuse feedstocks are tabulated in Appendix 7.

The solids that had passed through the reactor during the newsprint hydrolysis experiments were also analysed quantitatively for (residual) cellulose content. In order to do this, it was necessary to separate the solids from the hydrolysate, while trying to ensure that all the sugar had been rinsed from them and that they could be easily dissolved after drying. This was done by decanting the supernatant liquid from a sample bottle of hydrolysate (after an aliquot had been removed for glucose analysis), washing the solids into a centrifuge tube, and repeatedly spinning down the slurry, removing the supernatant liquid, and resuspending the centifuged solids with distilled water. The solids were then dried, weighed, and ground prior to cellulose determination. As the samples were small, the entire sample was always subjected to quantitative saccharification. The cellulosic content was expressed as a percentage of the original cellulose content of the slurry.

APPENDIX 2

CALCULATION OF REYNOLDS NUMBERS

In the calculations below, the properties of the slurry are assumed to be identical with those of water. This is a reasonable assumption, as the concentration of the slurry was low (below 0.3%) in all the experiments.

The temperature of the slurry as it passed through the rig varied from room temperature (say 20°C) to up to 240°C during the final four series of experiments (reported in Chapter 5), or from 90° to up to 240°C during the preliminary experiments using the large diameter preheating coil (reported in Chapter 4). The Reynolds numbers are calculated for the maximum and minimum temperatures in both cases, and at 180°C.

$$N_{Re} = \frac{D.v.\rho}{\mu}$$

$$= 4m/(\pi\mu D)$$

$$= 4m/(\pi\nu\rho D)$$

where D = inside diameter of pipe, m

v = linear velocity, m/sec

ρ = fluid density, kg/m^3

μ = fluid dynamic viscosity, kg/(m.sec)

ν = fluid kinematic viscosity, m^2/sec

m = fluid mass flow rate, kg/sec

from Wong (1977), the following properties of water may be found:

at 20°C, ρ = 1000.52 kg/m^3 ν = 10.06 x 10^{-7} m^2/sec
at 90°C, ρ = 967.36 kg/m^3 ν = 3.29 x 10^{-7} m^2/sec
at 180°C, ρ = 889.03 kg/m^3 ν = 1.73 x 10^{-7} m^2/sec
at 240°C, ρ = 815.66 kg/m^3 ν = 1.43 x 10^{-7} m^2/sec

For the large diameter tubing, D = 0.019 m
For the small diameter tubing, D = 0.00452 m

Substituting these values into the formula, the Reynolds numbers of the fluid in the small and large diameter tubing at the various temperatures and at a flow rate of 16.0 l/hr may be found to be:

For the small tubing:

N_{Re} = 1244 at 20°c
3805 at 90°C
7236 at 180°C
8755 at 240°C

For the large tubing:

N_{Re} = 296 at 20°C
905 at 90°C
1722 at 180°C
2083 at 240°C

APPENDIX 3

TABLES OF RESULTS

In the next ten pages, the following tables of results are set out:

Table A.3.1

Detailed results of filter paper hydrolysis tests

RUN NO	FEED ACID CONC %	FEED SLURRY CONC %	FEED FLOW RATE ml/min	CON FIG NO	TEMPERATURE A	B	C	D	E	F	RESIDENCE TIME (seconds) 1	2	3	4	5	6	HYDROLYSATE RES CELL %	GLUC CONC mg/dl	GLUC CONV %	DECOMP PROD %	TYPE OF SAMPLE
50	0.51	0.096	275	3	173	206	226	222	218	-	6.67	6.67	6.10	4.24	1.69	--	--	18.1	17.0	--	avg. 5 inst.
50	0.51	0.096	275	3	175	209	228	226	221	-	6.67	6.67	6.10	4.24	1.69	--	84.2	20.0	18.8	***	cumulative
50	0.51	0.096	275	3	176	210	229	228	224	-	6.67	6.67	6.10	4.24	1.69	--	76.4	20.0	18.8	4.8	cumulative
51	0.51	0.096	270	2	179	207	224	223	-	-	6.79	6.79	6.22	1.72	--	--	--	17.6	16.6	--	avg. 5 inst.
51	0.51	0.096	270	2	178	208	224	224	-	-	6.79	6.79	6.22	1.72	--	--	79.5	18.0	16.9	3.6	cumulative
51	0.51	0.096	235	2	190	221	227	233	-	-	7.81	7.81	7.14	1.98	--	--	68.3	26.0	24.5	7.2	cumulative
51	0.51	0.096	235	2	193	226	232	238	-	-	7.81	7.81	7.14	1.98	--	--	--	32.6	30.7	--	avg. 5 inst.
51	0.51	0.096	245	2	193	226	232	238	-	-	7.49	7.49	6.85	1.90	--	--	59.3	33.0	31.0	9.7	cumulative
52	0.51	0.096	283	1	174	201	236	223	-	-	6.48	6.48	2.76	0.98	--	--	--	13.8	13.0	--	avg. 5 inst.
52	0.51	0.096	285	1	168	194	227	217	-	-	6.44	6.44	2.74	0.98	--	--	87.3	8.0	7.5	5.2	cumulative
52	0.51	0.096	285	1	174	202	238	225	-	-	6.44	6.44	2.74	0.98	--	--	--	15.0	14.1	--	avg. 5 inst.
52	0.51	0.096	285	1	174	202	236	225	-	-	6.44	6.44	2.74	0.98	--	--	81.1	13.0	12.2	6.7	cumulative
53	0.97	0.188	295	1	167	197	222	220	-	-	6.22	6.22	2.65	0.94	--	--	78.3	38.0	18.2	3.5	cumulative
53	0.97	0.188	295	1	165	196	220	219	-	-	6.22	6.22	2.65	0.94	--	--	--	34.4	16.4	--	avg. 5 inst.
53	0.97	0.188	295	1	167	199	224	222	-	-	6.22	6.22	2.65	0.94	--	--	--	40.8	19.5	--	avg. 5 inst.
53	0.97	0.188	295	1	170	202	227	225	-	-	6.22	6.22	2.65	0.94	--	--	71.9	46.0	22.0	6.1	cumulative
53	0.97	0.188	270	1	176	213	234	233	-	-	6.79	6.79	2.90	1.03	--	--	59.2	64.0	30.6	10.2	cumulative
53	0.97	0.188	270	1	181	215	234	233	-	-	6.79	6.79	2.90	1.03	--	--	--	60.6	29.0	--	avg. 5 inst.

Table A.3.1 (continued)
Detailed results of filter paper hydrolysis tests

RUN NO	FEED ACID CONC %	FEED SLURRY CONC %	FEED FLOW RATE ml/min	CON FIG NO	TEMPERATURE A	B	C	D	E	F	RESIDENCE TIME (seconds) 1	2	3	4	5	6	HYDROLYSATE RES CELL %	GLUC CONC mg/dl	GLUC CONV %	DECOMP PROD %	TYPE OF SAMPLE
54	1.00	0.191	255	1	178	201	227	225	-	-	7.19	7.19	3.07	1.09	--	--	73.2	53.0	25.0	1.8	cumulative
54	1.00	0.191	260	1	179	203	228	227	-	-	7.05	7.05	3.01	1.07	--	--	--	52.2	24.7	--	avg. 5 inst.
54	1.00	0.191	265	1	179	203	229	228	-	-	6.92	6.92	2.95	1.05	--	--	71.0	56.0	26.4	2.6	cumulative
54	1.00	0.191	245	1	188	208	233	233	-	-	7.49	7.49	3.19	1.14	--	--	--	64.0	30.2	--	avg. 5 inst.
54	1.00	0.191	245	1	191	221	240	240	-	-	7.49	7.49	3.19	1.14	--	--	--	87.5	41.3	--	avg. 5 inst.
54	1.00	0.191	240	1	190	220	239	239	-	-	7.64	7.64	3.26	1.16	--	--	42.0	85.0	40.1	17.9	cumulative
54	1.00	0.191	245	1	192	219	240	240	-	-	7.49	7.49	3.19	1.14	--	--	--	83.6	39.5	--	avg. 5 inst.
54	1.00	0.191	245	1	195	220	240	240	-	-	7.49	7.49	3.19	1.14	--	--	46.1	85.0	40.1	13.8	cumulative
55	1.00	0.191	310	2	163	194	212	205	-	-	5.92	5.92	5.41	1.50	--	--	87.4	30.0	14.2	***	cumulative
55	1.00	0.191	310	2	160	191	211	201	-	-	5.92	5.92	5.41	1.50	--	--	--	28.0	13.2	--	avg. 5 inst.
55	1.00	0.191	255	2	178	212	222	212	-	-	7.19	7.19	6.58	1.82	--	--	74.5	53.0	25.0	0.5	cumulative
55	1.00	0.191	255	2	175	209	221	208	-	-	7.19	7.19	6.58	1.82	--	--	--	50.8	24.0	--	avg. 5 inst.
55	1.00	0.191	250	2	189	226	230	223	-	-	7.34	7.34	6.71	1.86	--	--	56.1	72.0	34.0	9.9	cumulative
55	1.00	0.191	250	2	184	219	227	218	-	-	7.34	7.34	6.71	1.86	--	--	--	67.4	31.8	--	avg. 5 inst.
56	0.49	0.092	270	4	171	202	219	218	217	211	6.79	6.79	6.22	4.32	4.32	1.72	79.7	12.0	11.7	8.6	cumulative
56	0.49	0.092	270	4	172	206	219	219	219	214	6.79	6.79	6.22	4.32	4.32	1.72	--	14.2	13.9	--	avg. 5 inst.
57	0.49	0.091	265	5	181	212	227	225	221	215	6.92	6.92	6.33	4.40	4.40	6.15	75.9	21.0	20.9	3.2	cumulative
57	0.49	0.091	265	5	181	213	227	226	222	216	6.92	6.92	6.33	4.40	4.40	6.15	--	19.6	19.5	--	avg. 5 inst.
57	0.49	0.091	270	5	180	200	219	213	211	+++	6.79	6.79	6.22	4.32	4.32	6.04	79.3	14.0	13.9	6.8	cumulative

Table A.3.1 (continued)
Detailed results of filter paper hydrolysis tests

RUN NO	FEED ACID CONC %	FEED SLURRY CONC %	FEED FLOW RATE ml/min	CON FIG NO	TEMPERATURE A	B	C	D	E	F	RESIDENCE TIME (seconds) 1	2	3	4	5	6	HYDROLYSATE RES CELL %	GLUC CONC mg/dl	GLUC CONV %	DECOMP PROD %	TYPE OF SAMPLE
57	0.49	0.091	270	5	180	200	219	213	211	+++	6.79	6.79	6.22	4.32	4.32	6.04	--	14.0	13.9	--	avg. 5 inst.
57	0.49	0.091	278	5	179	197	211	206	203	+++	6.60	6.60	6.04	4.19	4.19	5.86	75.1	9.0	8.9	16.0	cumulative
57	0.49	0.091	278	5	180	197	211	206	203	+++	6.60	6.60	6.04	4.19	4.19	5.86	--	10.0	9.9	--	avg. 5 inst.
58	1.01	0.190	285	5	176	200	216	210	207	+++	6.44	6.44	5.89	4.09	4.09	5.72	79.3	44.0	20.9	***	cumulative
58	1.01	0.190	285	5	175	200	217	210	207	+++	6.44	6.44	5.89	4.09	4.09	5.72	--	44.8	21.2	--	avg. 5 inst.
58	1.01	0.190	285	5	176	203	224	219	216	+++	6.44	6.44	5.89	4.09	4.09	5.72	70.1	58.0	27.5	2.4	cumulative
58	1.01	0.190	285	5	175	204	226	220	217	+++	6.44	6.44	5.89	4.09	4.09	5.72	--	61.8	29.3	--	avg. 5 inst.
58	1.01	0.190	285	5	174	195	209	204	201	+++	6.44	6.44	5.89	4.09	4.09	5.72	83.2	35.0	16.6	0.2	cumulative
58	1.01	0.190	285	5	174	195	208	203	200	+++	6.44	6.44	5.89	4.09	4.09	5.72	--	33.4	15.8	--	avg. 5 inst.
59	1.01	0.189	260	4	175	200	220	215	211	205	7.05	7.05	6.45	4.48	4.48	1.79	74.1	46.0	21.9	4.0	cumulative
59	1.01	0.189	260	4	173	198	221	215	211	205	7.05	7.05	6.45	4.48	4.48	1.79	--	52.4	25.0	--	avg. 5 inst.
59	1.01	0.189	310	4	176	200	227	222	219	212	5.92	5.92	5.41	3.76	3.76	1.50	67.1	63.0	30.0	2.9	cumulative
59	1.01	0.189	275	4	177	198	228	223	220	213	6.67	6.67	6.10	4.24	4.24	1.69	--	66.6	31.7	--	avg. 5 inst.
59	1.01	0.189	275	4	176	197	228	224	220	213	6.67	6.67	6.10	4.24	4.24	1.69	62.6	66.0	31.5	5.9	cumulative
59	1.01	0.189	290	4	175	186	215	209	206	201	6.33	6.33	5.79	4.02	4.02	1.60	80.6	43.0	20.5	***	cumulative
59	1.01	0.189	290	4	175	186	214	209	206	200	6.33	6.33	5.79	4.02	4.02	1.60	--	41.8	19.9	--	avg. 5 inst.
60	1.01	0.188	280	3	166	182	218	211	206	-	6.55	6.55	5.99	4.16	1.66	--	75.7	41.0	19.6	4.7	cumulative
60	1.01	0.188	280	3	168	182	219	212	207	-	6.55	6.55	5.99	4.16	1.66	--	--	43.2	20.7	--	avg. 5 inst.
60	1.01	0.188	275	3	170	184	224	217	213	-	6.67	6.67	6.10	4.24	1.69	--	69.1	53.0	25.4	5.5	cumulative

Table A.3.1 (continued)
Detailed results of filter paper hydrolysis tests

	FEED				TEMPERATURE						RESIDENCE TIME (seconds)						HYDROLYSATE				
RUN NO	ACID CONC %	SLURRY CONC %	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	RES CELL %	GLUC CONC mg/dl	GLUC CONV %	DECOMP PROD %	TYPE OF SAMPLE
60	1.01	0.188	275	3	171	184	224	217	213	-	6.67	6.67	6.10	4.24	1.69	--	--	55.2	26.4	--	avg. 5 inst.
62	1.49	0.202	250	3	161	193	219	213	207	-	7.34	7.34	6.71	4.66	1.86	--	67.3	59.0	26.3	6.4	cumulative
62	1.49	0.202	290	3	160	196	223	215	210	-	6.33	6.33	5.79	4.02	1.60	--	--	71.4	31.8	--	avg. 5 inst.
62	1.49	0.202	290	3	163	201	226	220	214	-	6.33	6.33	5.79	4.02	1.60	--	56.7	77.0	34.3	9.0	cumulative
64	1.39	0.192	225	3	171	205	203	197	191	-	8.15	8.15	7.46	5.18	2.07	--	--	51.2	24.0	--	avg. 5 inst.
64	1.39	0.192	225	3	174	208	204	198	192	-	8.15	8.15	7.46	5.18	2.07	--	74.0	53.0	24.8	1.2	cumulative
64	1.39	0.192	245	3	181	215	212	205	201	-	7.49	7.49	6.85	4.76	1.90	--	73.4	61.0	28.6	***	cumulative
65	1.52	0.198	278	2	168	203	222	216	-	-	6.60	6.60	6.04	1.67	--	--	63.5	65.0	29.5	7.0	cumulative
65	1.52	0.198	278	2	167	202	223	217	-	-	6.60	6.60	6.04	1.67	--	--	--	68.8	31.3	--	avg. 5 inst.
65	1.52	0.198	285	2	169	205	229	222	-	-	6.44	6.44	5.89	1.63	--	--	49.2	88.0	40.0	10.8	cumulative
65	1.52	0.198	285	2	170	206	230	223	-	-	6.44	6.44	5.89	1.63	--	--	--	93.2	42.4	--	avg. 5 inst.
65	1.52	0.198	290	2	169	206	231	224	-	-	6.33	6.33	5.79	1.60	--	--	43.2	99.0	45.0	11.8	cumulative
65	1.52	0.198	290	2	168	205	233	227	-	-	6.33	6.33	5.79	1.60	--	--	--	103.8	47.2	--	avg. 5 inst.
65	1.52	0.198	285	2	169	206	233	227	-	-	6.44	6.44	5.89	1.63	--	--	38.5	105.0	47.7	13.8	cumulative
66	1.52	0.198	290	1	171	205	223	222	-	-	6.33	6.33	2.70	0.96	--	--	65.3	58.0	26.4	8.3	cumulative
66	1.52	0.198	290	1	170	205	225	223	-	-	6.33	6.33	2.70	0.96	--	--	--	63.8	29.0	--	avg. 5 inst.
66	1.52	0.198	283	1	174	208	229	227	-	-	6.48	6.48	2.76	0.98	--	--	55.7	81.0	36.8	7.5	cumulative
66	1.52	0.198	283	1	175	209	231	229	-	-	6.48	6.48	2.76	0.98	--	--	--	86.4	39.3	--	avg. 5 inst.

Table A.3.1 (continued)
Detailed results of filter paper hydrolysis tests

RUN NO	FEED ACID CONC %	FEED SLURRY CONC %	FEED FLOW RATE ml/min	CON FIG NO	TEMPERATURE A	B	C	D	E	F	RESIDENCE TIME (seconds) 1	2	3	4	5	6	HYDROLYSATE RES CELL %	GLUC CONC mg/dl	GLUC CONV %	DECOMP PROD %	TYPE OF SAMPLE
66	1.52	0.198	270	1	179	213	233	232	-	-	6.79	6.79	2.90	1.03	--	--	44.6	94.0	42.7	12.7	cumulative
69	1.48	0.090	285	5	176	211	212	209	203	197	6.44	6.44	5.89	4.09	4.09	5.72	71.6	23.0	23.0	5.4	cumulative
69	1.48	0.090	285	5	177	213	213	210	205	199	6.44	6.44	5.89	4.09	4.09	5.72	--	24.2	24.2	--	avg. 5 inst.
69	1.48	0.090	270	5	179	215	223	223	222	217	6.79	6.79	6.22	4.32	4.32	6.04	57.6	32.0	32.0	10.4	cumulative
69	1.48	0.090	270	5	178	215	224	224	223	218	6.79	6.79	6.22	4.32	4.32	6.04	--	35.0	35.0	--	avg. 5 inst.
69	1.48	0.090	260	5	186	226	231	231	231	231	7.05	7.05	6.45	4.48	4.48	6.27	--	44.8	44.8	--	avg. 5 inst.
69	1.48	0.090	260	5	188	227	231	232	232	232	7.05	7.05	6.45	4.48	4.48	6.27	35.8	45.0	45.0	19.2	cumulative
70	1.48	0.090	280	4	177	214	216	213	207	201	6.55	6.55	5.99	4.16	4.16	1.66	66.1	29.0	29.0	4.9	cumulative
70	1.48	0.090	280	4	179	214	216	213	208	202	6.55	6.55	5.99	4.16	4.16	1.66	--	31.0	31.0	--	avg. 5 inst.
70	1.48	0.090	285	4	181	217	226	225	224	218	6.44	6.44	5.89	4.09	4.09	1.63	54.3	39.0	39.0	6.7	cumulative
70	1.48	0.090	285	4	179	215	226	226	224	218	6.44	6.44	5.89	4.09	4.09	1.63	--	39.6	39.6	--	avg. 5 inst.
70	1.48	0.090	273	4	189	225	233	233	234	233	6.72	6.72	6.15	4.27	4.27	1.70	32.4	45.0	45.0	22.6	cumulative
70	1.48	0.090	273	4	188	226	234	234	234	233	6.72	6.72	6.15	4.27	4.27	1.70	--	46.2	46.2	--	avg. 5 inst.

Table A.3.2

Detailed results of newsprint hydrolysis tests

	FEED				TEMPERATURE						RESIDENCE TIME (seconds)						HYDROLYSATE			
RUN NO	ACID CONC %	SLURRY CONC %	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	RES CELL %	GLUC CONC mg/dl	GLUC CONV %	DECOMP PROD %
86	1.48	0.209	285	1	169	199	195	194	-	-	6.44	6.44	2.74	0.98	--	--	85.6	40.5	32.3	**
86	1.48	0.209	280	1	174	208	216	214	-	-	6.55	6.55	2.79	0.99	--	--	37.6	58.8	46.9	15.5
86	1.48	0.209	270	1	179	214	227	226	-	-	6.79	6.79	2.90	1.03	--	--	11.8	78.0	62.2	26.0
86	1.48	0.209	265	1	183	218	236	235	-	-	6.92	6.92	2.95	1.05	--	--	8.8	89.3	71.3	19.9
87(a)	1.00	0.141	270	1	169	199	196	194	-	-	6.79	6.79	2.90	1.03	--	--	72.1	22.7	27.2	0.7
87(a)	1.00	0.141	275	1	171	207	217	216	-	-	6.67	6.67	2.84	1.01	--	--	52.2	35.8	42.9	4.9
87(a)	1.00	0.141	265	1	174	209	226	226	-	-	6.92	6.92	2.95	1.05	--	--	44.2	44.0	52.7	3.1
87(a)	1.00	0.141	255	1	183	218	235	236	-	-	7.19	7.19	3.07	1.09	--	--	15.3	58.1	69.6	15.1
87(b)	0.50	0.070	280	1	173	210	215	214	-	-	6.55	6.55	2.79	0.99	--	--	59.7	13.2	31.6	8.7
87(b)	0.50	0.070	280	1	176	214	224	224	-	-	6.55	6.55	2.79	0.99	--	--	47.0	16.4	39.3	13.7
87(b)	0.50	0.070	255	1	185	222	236	236	-	-	7.19	7.19	3.07	1.09	--	--	31.2	24.0	57.5	11.3
88(a)	1.47	0.214	300	5	175	201	199	192	187	183	6.11	6.11	9.47	3.88	3.88	1.55	73.9	43.2	33.8	**
88(a)	1.47	0.214	280	5	177	212	215	215	213	209	6.55	6.55	10.15	4.16	4.16	1.66	49.8	67.6	52.9	**
88(a)	1.47	0.214	275	5	184	219	223	223	223	221	6.67	6.67	10.34	4.24	4.24	1.69	12.3	81.3	63.7	14.0
88(a)	1.47	0.214	255	5	201	230	230	231	231	231	7.19	7.19	11.15	4.57	4.57	1.82	7.8	89.7	70.3	21.9
88(b)	0.99	0.137	260	5	193	218	217	217	217	217	7.05	7.05	10.93	4.48	4.48	1.79	--	44.8	54.6	--
88(b)	0.99	0.137	245	5	195	225	226	226	226	226	7.49	7.49	11.61	4.76	4.76	1.90	--	57.6	70.2	--
88(b)	0.99	0.137	245	5	203	231	231	231	231	231	7.49	7.49	11.61	4.76	4.76	1.90	--	60.9	74.3	--

Table A.3.2 (continued)
Detailed results of newsprint hydrolysis tests

	FEED																HYDROLYSATE			
					TEMPERATURE						RESIDENCE TIME (seconds)									
RUN NO	ACID CONC %	SLURRY CONC %	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	RES CELL %	GLUC CONC mg/dl	GLUC CONV %	DECOMP PROD %
88(c)	0.49	0.068	260	5	190	218	217	217	217	218	7.05	7.05	10.93	4.48	4.48	1.79	--	18.5	45.4	--
88(c)	0.49	0.068	250	5	200	224	223	223	223	223	7.34	7.34	11.37	4.66	4.66	1.86	--	22.8	55.9	--
88(c)	0.49	0.068	250	5	201	228	227	227	227	227	7.34	7.34	11.37	4.66	4.66	1.86	--	26.0	63.8	--
89(a)	1.47	0.211	290	3	169	198	194	189	183	-	6.33	6.33	5.79	4.02	1.60	--	--	41.7	33.1	--
89(a)	1.47	0.211	280	3	174	209	214	208	202	-	6.55	6.55	5.99	4.16	1.66	--	--	62.7	49.7	--
89(a)	1.47	0.211	280	3	177	212	226	220	213	-	6.55	6.55	5.99	4.16	1.66	--	--	81.8	64.9	--
89(a)	1.47	0.211	280	3	179	214	234	228	222	-	6.55	6.55	5.99	4.16	1.66	--	--	87.8	69.7	--
89(b)	1.00	0.139	290	3	173	208	216	211	206	-	6.33	6.33	5.79	4.02	1.60	--	--	42.8	51.4	--
89(b)	1.00	0.139	285	3	177	212	224	218	213	-	6.44	6.44	5.89	4.09	1.63	--	--	51.0	61.3	--
89(b)	1.00	0.139	270	3	182	217	235	233	228	-	6.79	6.79	6.22	4.32	1.72	--	--	60.4	72.6	--
90	0.50	0.076	292	3	176	210	215	210	205	-	6.28	6.28	5.74	3.99	1.59	--	--	18.6	41.0	--
90	0.50	0.076	280	3	183	215	226	221	216	-	6.55	6.55	5.99	4.16	1.66	--	--	21.8	48.0	--
90	0.50	0.076	265	3	190	218	234	234	231	-	6.92	6.92	6.33	4.40	1.75	--	--	25.0	55.0	--

Table A.3.3
Detailed results of refuse hydrolysis tests

RUN NO	FEED ACID CONC %	FEED SLURRY CONC %	FLOW RATE ml/ min	CON FIG NO	TEMPERATURE A	B	C	D	E	F	RESIDENCE TIME (seconds) 1	2	3	4	5	6	HYDROLYSATE RES SOLID %	GLUC CONC mg/dl	GLUC CONV %
93	1.46	0.200	313	1	170	205	226	223	-	-	5.86	5.86	2.50	0.89	--	--	45.3	50.0	50.6
93	1.46	0.200	313	1	173	211	230	227	-	-	5.86	5.86	2.50	0.89	--	--	38.5	55.1	56.2
93	1.46	0.200	287	1	175	215	233	230	-	-	6.39	6.39	2.72	0.97	--	--	32.8	60.1	60.8
94	0.99	0.131	295	1	170	200	219	218	-	-	6.22	6.22	2.65	0.94	--	--	52.3	24.0	37.1
94	0.99	0.131	288	1	186	212	227	227	-	-	6.37	6.37	2.71	0.97	--	--	44.7	35.8	55.3
94	0.99	0.131	255	1	188	217	234	234	-	-	7.19	7.19	3.07	1.09	--	--	37.3	43.8	67.7
95	0.99	0.131	295	3	175	207	221	222	219	-	6.22	6.22	5.69	3.95	1.58	--	49.1	32.1	49.6
95	0.99	0.131	275	3	197	219	228	229	228	-	6.67	6.67	6.10	4.24	1.69	--	39.8	40.1	62.0
95	0.99	0.131	268	3	198	225	232	233	232	-	6.84	6.84	6.26	4.35	1.73	--	33.8	43.5	67.2
96	1.43	0.199	260	3	187	211	219	219	217	-	7.05	7.05	6.45	4.48	1.79	--	48.2	53.9	54.8
96	1.43	0.199	260	3	199	216	226	226	226	-	7.05	7.05	6.45	4.48	1.79	--	37.9	59.0	60.0
96	1.43	0.199	250	3	199	228	231	232	232	-	7.34	7.34	6.71	4.66	1.86	--	29.7	61.3	62.4
97a	1.43	0.199	280	5	190	214	217	217	217	215	6.55	6.55	10.15	4.16	4.16	1.66	52.0	49.0	49.9
97a	1.43	0.199	255	5	202	226	226	226	227	227	7.19	7.19	11.15	4.57	4.57	1.82	40.2	60.3	61.4
97a	1.43	0.199	235	5	217	230	230	230	230	230	7.81	7.81	12.10	4.96	4.96	1.98	29.8	61.2	62.3
97b	0.95	0.130	272	5	195	209	209	209	209	207	6.74	6.74	10.45	4.28	4.28	1.71	62.5	25.9	40.3
97b	0.95	0.130	277	5	190	216	216	216	216	216	6.62	6.62	10.26	4.21	4.21	1.68	57.2	29.4	45.8
97b	0.95	0.130	250	5	200	223	223	223	224	224	7.34	7.34	11.37	4.66	4.66	1.86	47.5	36.3	56.5
97b	0.95	0.130	265	5	206	228	228	227	228	228	6.92	6.92	10.73	4.40	4.40	1.75	39.0	38.3	59.7

Table A.3.4
Detailed results of glucose decomposition tests

RUN NO	FEED ACID CONC %	FEED GLUC CONC mg/dl	FLOW RATE ml/ min	CON FIG NO	TEMPERATURE A	B	C	D	E	F	RESIDENCE TIME (seconds) 1	2	3	4	5	6	PRODUCT GLUC CONC mg/dl	GLUC DECOMP %	RES GLUC %
83(a)	1.47	297	230	3	191	193	187	179	172	-	7.97	7.97	7.30	5.07	2.02	--	254	14.5	85.5
83(a)	1.47	297	245	3	197	207	210	193	186	-	7.49	7.49	6.85	4.76	1.90	--	222	25.3	74.7
83(a)	1.47	297	240	3	198	220	217	210	203	-	7.64	7.64	6.99	4.86	1.94	--	159	46.3	53.7
83(a)	1.47	297	225	3	206	224	229	226	218	-	8.15	8.15	7.46	5.18	2.07	--	109	63.4	36.6
83(a)	1.47	297	215	3	215	228	237	236	235	-	8.53	8.53	7.81	5.42	2.16	--	77	74.0	26.0
83(b)	1.01	209	250	3	197	206	202	196	190	-	7.34	7.34	6.71	4.66	1.86	--	151	27.7	72.3
83(b)	1.01	209	245	3	201	221	221	211	205	-	7.49	7.49	6.85	4.76	1.90	--	113	46.1	53.9
83(b)	1.01	209	235	3	209	227	226	223	216	-	7.81	7.81	7.14	4.96	1.98	--	95	54.3	45.7
83(b)	1.01	209	215	3	217	232	235	234	233	-	8.53	8.53	7.81	5.42	2.16	--	68	67.6	32.4
83(c)	0.50	101	250	3	195	202	198	192	187	-	7.34	7.34	6.71	4.66	1.86	--	84	17.3	82.7
83(c)	0.50	101	215	3	194	220	216	208	202	-	8.53	8.53	7.81	5.42	2.16	--	68	32.6	67.4
83(c)	0.50	101	230	3	200	226	226	224	216	-	7.97	7.97	7.30	5.07	2.02	--	55	45.8	54.2
83(c)	0.50	101	235	3	213	232	235	234	234	-	7.81	7.81	7.14	4.96	1.98	--	39	61.1	38.9
84(a)	0.49	401.5	230	5	188	206	201	190	185	180	7.97	7.97	12.37	5.07	5.07	2.02	352	12.4	87.6
84(a)	0.49	401.5	260	5	189	215	214	206	201	194	7.05	7.05	10.93	4.48	4.48	1.79	315	21.5	78.5
84(a)	0.49	401.5	250	5	197	225	226	226	226	223	7.34	7.34	11.37	4.66	4.66	1.86	224	44.2	55.8
84(a)	0.49	401.5	225	5	206	233	233	233	233	233	8.15	8.15	12.64	5.18	5.18	2.07	156	61.1	38.9
84(b)	1.45	398.5	245	5	186	189	187	179	175	171	7.49	7.49	11.61	4.76	4.76	1.90	340	14.8	85.2
84(b)	1.45	398.5	230	5	189	203	199	189	183	178	7.97	7.97	12.37	5.07	5.07	2.02	310	22.3	77.7
84(b)	1.45	398.5	245	5	192	217	215	210	204	198	7.49	7.49	11.61	4.76	4.76	1.90	239	40.1	59.9
84(b)	1.45	398.5	230	5	206	227	227	227	226	223	7.97	7.97	12.37	5.07	5.07	2.02	153	61.7	38.3
84(b)	1.45	398.5	220	5	213	235	235	235	235	235	8.34	8.34	12.92	5.30	5.30	2.11	121	69.6	30.4

Table A.3.4 (continued)
Detailed results of glucose decomposition tests

RUN NO	FEED ACID CONC %	FEED GLUC CONC mg/dl	FLOW RATE ml/ min	CON FIG NO	TEMPERATURE A	B	C	D	E	F	RESIDENCE TIME (seconds) 1	2	3	4	5	6	PRODUCT GLUC CONC mg/dl	GLUC DECOMP %	RES GLUC %
84(c)	0.95	261	235	5	190	197	195	185	181	177	7.81	7.81	12.10	4.96	4.96	1.98	224	14.3	85.7
84(c)	0.95	261	240	5	198	216	216	214	208	202	7.64	7.64	11.85	4.86	4.86	1.94	170	34.9	65.1
84(c)	0.95	261	232	5	204	226	225	225	225	222	7.91	7.91	12.26	5.02	5.02	2.00	121	53.5	46.5
84(c)	0.95	261	225	5	213	234	233	233	233	233	8.15	8.15	12.64	5.18	5.18	2.07	83	68.1	31.9
85(a)	1.46	302	252	1	182	187	182	180	-	-	7.28	7.28	3.10	1.10	--	--	264	12.6	87.4
85(a)	1.46	302	248	1	189	206	201	199	-	-	7.40	7.40	3.15	1.12	--	--	236	21.9	78.1
85(a)	1.46	302	238	1	195	223	220	219	-	-	7.71	7.71	3.28	1.17	--	--	152	49.7	50.3
85(a)	1.46	302	230	1	200	226	230	230	-	-	7.97	7.97	3.40	1.21	--	--	122	59.6	40.4
85(a)	1.46	302	230	1	207	230	237	237	-	-	7.97	7.97	3.40	1.21	--	--	87	71.2	28.8
85(b)	0.96	199	245	1	187	202	199	198	-	-	7.49	7.49	3.19	1.14	--	--	163	18.1	81.9
85(b)	0.96	199	245	1	193	223	220	219	-	-	7.49	7.49	3.19	1.14	--	--	121	39.2	60.8
85(b)	0.96	199	245	1	199	226	228	228	-	-	7.49	7.49	3.19	1.14	--	--	98	50.8	49.2
85(b)	0.96	199	220	1	205	228	234	235	-	-	8.34	8.34	3.55	1.27	--	--	80	59.8	40.2
85(c)	0.48	98	247	1	191	202	199	198	-	-	7.43	7.43	3.17	1.13	--	--	82	16.3	83.7
85(c)	0.48	98	255	1	189	218	215	213	-	-	7.19	7.19	3.07	1.09	--	--	71	27.6	72.4
85(c)	0.48	98	240	1	199	223	226	227	-	-	7.64	7.64	3.26	1.16	--	--	57	41.8	58.2
85(c)	0.48	98	233	1	203	224	234	235	-	-	7.87	7.87	3.36	3.97	--	--	47	52.0	48.0

APPENDIX 4

SAMPLE CALCULATIONS

A.4.1 Slurry feed

For each hydrolysis run, duplicate samples of the unreacted slurry were analysed for solids content and acid concentration. The samples were taken from the outlet valve of the feed tank in previously weighed bottles. The bottles were weighed again, and the solids filtered using Whatman GF/A glass microfibre filters. The solids were then oven dried, weighed, and expressed as a percentage of the original sample weight. It was necessary to use glass microfibre filters as filter paper loses moisture on oven drying and would have produced erroneous results.

The filtrates from these samples were used for the determination of acid concentration. Aliquots of 50 ml were neutralised to pH 6 with 1 N sodium hydroxide (made up using "Volucon" standard volumetric concentrate ampoules). A Corning Model 12 pH meter was used to monitor the course of the titrations, the samples being stirred continuously with the aid of a magnetic stirrer. The resulting acid concentrations were expressed as weight percent sulphuric acid, as follows:

Run 97(a)

Volume of 1 N NaOH required
to neutralise 50 ml feed sample = 14.70 ml

$$\text{thus normality of acid in feed} = \frac{14.70 \times 1}{50}$$

$$= 0.294 \text{ N } H_2SO_4$$

to convert this to weight percent :

$$0.294\ N\ H_2SO_4 = 0.294\ eq.\ H_2SO_4/l \text{ of solution}$$

$$= 0.294 \times 49.04\ g\ H_2SO_4/l \text{ of solution}$$

$$= \frac{0.294 \times 49.04}{10}\ g\ H_2SO_4/100\ ml \text{ of solution}$$

$$= 1.442\ g\ H_2SO_4/100\ ml \text{ of solution}$$

$$= 0.786\ ml\ H_2SO_4/100\ ml \text{ of solution}$$

(S.G.=1.835)

The remainder is water, i.e. 99.214 ml water

or approximately 99.214 g water

So the concentration of acid is

$$1.442/(1.442 + 99.214) = 1.43\ \%\ H_2SO_4$$

A.4.2 Hydrolysate

Cumulative samples of hydrolysate were collected in a measuring cylinder over a period of one minute, and transferred to 500 ml sample bottles, which had been previously weighed. These samples were analysed for glucose, residual solids content (filter paper, refuse) and residual cellulose content (newsprint). During the filter paper runs, spot samples were also taken, in 5 ml disposable test tubes. These were analysed for glucose content only. Glucose, residual solids and residual cellulose content were expressed, respectively, as a percentage of the original (potential) glucose, solids or cellulose content in the unreacted slurry. The following example describes the procedure and calculations for a typical sample of newsprint hydrolysate.

Run 86 (newsprint)

sample bottle 111: max temp 214°C flow rate: 280ml/min

Once the solids had settled, a 50 ml sample of the supernatant liquid was drawn off and neutralised to pH 6 with 1N NaOH. (This caused the decomposition products, like hydroxymethylfurfural, to be precipitated out of solution). A 25 microlitre sample of the neutralised solution was then taken with the Syringepet for glucose analysis in the YSI Industrial Analyser. The cellulose content of the residual solids (in the original hydrolysate sample) was determined by the quantitative saccharification method described in Appendix 1.2.

Volume of 1 N NaOH required
to neutralise 50 ml feed sample = 13.95 ml

glucose content of neutralised solution = 49 mg/dl
(by Glucose Analyser)

thus glucose content of hydrolysate = 49 x (50 + 13.95)/50
= 62.7 mg/dl

Feed slurry concentration = 0.211%
= 0.211 mg newsprint/100 mg slurry feed

Cellulose content in newsprint = 53.7%
Thus cellulose in feed slurry = (0.537 x 0.211)/100 mg cellulose per mg feed
= 1.133 mg cellulose/ g feed
So potential glucose in feed = 1.133 x (180/162) mg/ mg feed
= 1.259 mg/ g feed
or (approximately) 1.259 mg/ ml feed
= 125.9 mg/dl

Thus conversion of celulose to glucose during hydrolysis is

(62.7/125.9) x 100 = 49.7 %

The residual solids remaining after hydrolysis in sample bottle 111 were recovered, dried and subjected to quantitative saccharification (as described in Appendix 1.2). The end result of this procedure was a 250 ml solution of glucose representing the cellulose content of the residual solids. A 25 ml sample of this solution was neutralised with NaOH to pH 6, and analysed for glucose. From this was calculated the amount of glucose contained in the 250 ml solution, as follows:

Volume of 1 N NaOH required
to neutralise 25 ml of solution = 11.2 ml

glucose content of neutralised solution = 51 mg/dl

glucose content after volumetric correction = (51 x 36.2)/25

= 73.8 mg/dl

This is contained in 250 ml, ie in 2.5 dl of solution

Thus the total mass of glucose in solution = 73.8 x 2.5
= 184.6 mg

This represents the cellulose content in the residual solids, which were contained in 281.3 g of hydrolysate sample (weight of sample bottle full - weight empty). Thus the residual cellulose content of the hydrolysate, expressed as potential glucose, is

(184.6/281.3) mg/g hydrolysate

or approximately 0.656 mg/ml hydrolysate

= 65.6 mg/dl hydrolysate

The cellulose content of unreacted slurry, expressed as potential glucose, has already been calculated to be 125.9 mg/dl (see above). The residual cellulose content in the solids in the hydrolysate is thus

$(65.6/125.9) \times 100 = \underline{52.1\%}$

A.4.3 Temperature

During each run, the temperature at various points in the rig was measured with the aid of thermocouple probes inserted into the slurry flow, and recorded continuously onto cassette tape using a Datalogger. What was actiually recorded onto tape was a series of mV readings, which needed to be calibrated after the run into ^{o}C. In order to do this, one set of thermocouple wires was also connected to the mV meter, which was specially calibrated for use with NiCr/NiAl thermocouples, and whose scale was in ^{o}C.

At the beginning of each run, a note was made of the time when the Datalogger was switched on, and during the run the temperature reading produced by the thermocouple connected to the mV meter would be noted and written down at intervals. A note was also made of the exact time that each sample was taken.

After the run, the list of temperatures which had been recorded manually (typically 20 to 30 points per run) were matched with the mV readings recorded by the Datalogger for that thermocouple at the same moments in time, and a regression equation temperature=f(mV) worked out. This equation was then used to translate all the mV readings on the cassette into temperatures in ^{o}C.

The thermocouple:mV-meter combination had been previously calibrated over the temperature range 180^{o} to $240^{o}C$, in an oil bath, against a precision mercury thermometer graduated in increments of $0.2^{o}C$. The calibration curve is shown in Figure A.5.1: the equation of the curve was found by linear regression to be $y=0.96x + 4.2$, where x is the temperature as measured on the mV meter, and y the accurate temperature measurement on the precision thermometer. All the readings produced from the Datalogger data had therefor to be corrected according to this equation.

There was one other complication. When calculating the temperatures at various points along the rig associated with each hydrolysate sample,

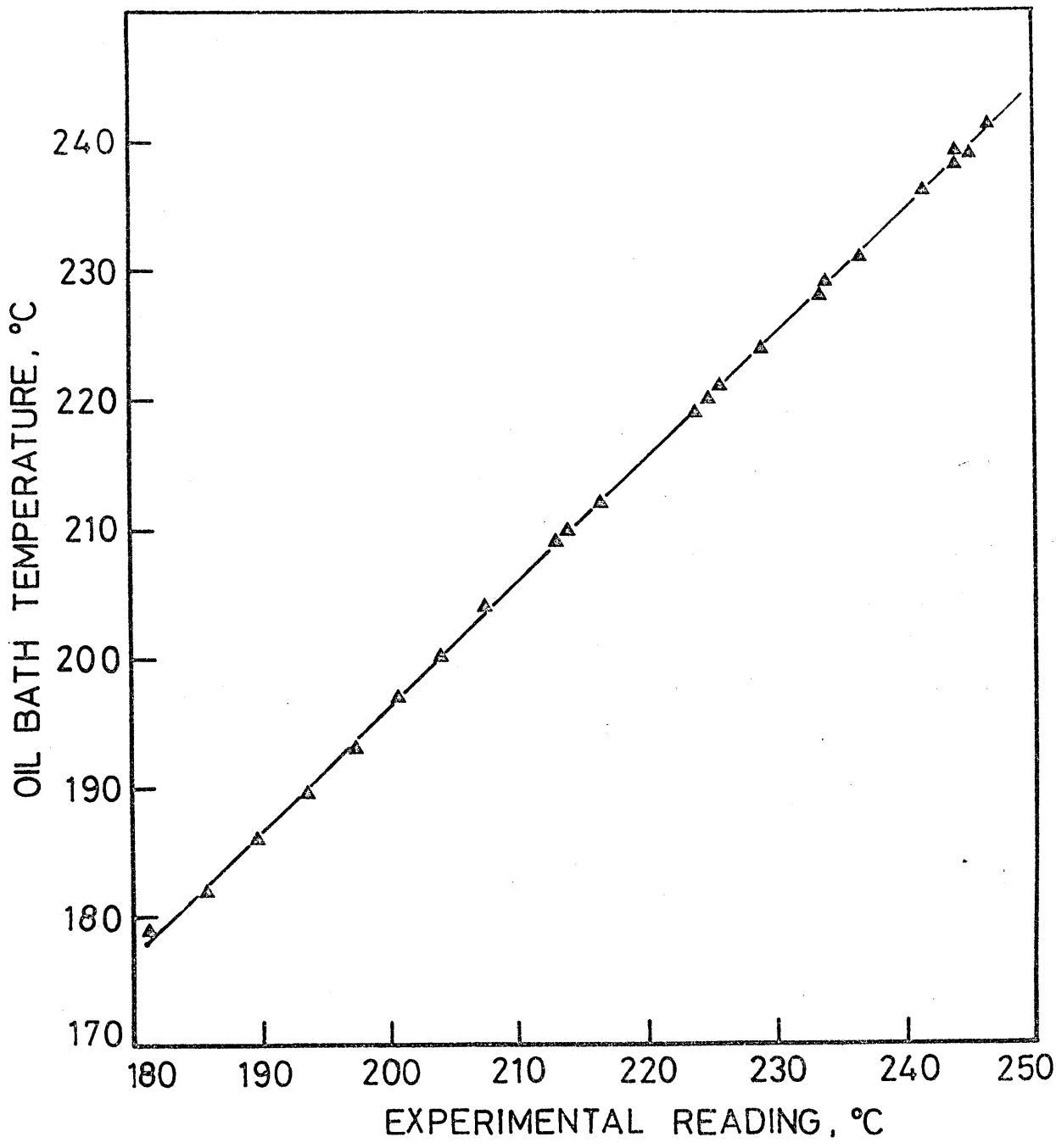
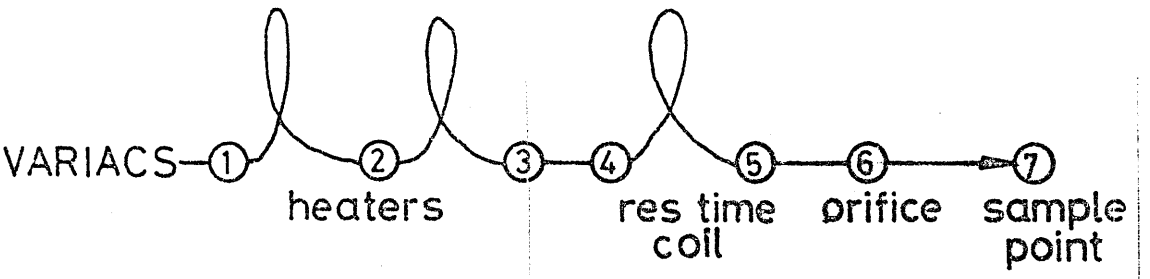


Figure A.4.1 Temperature correction curve for mV-meter.

allowance had to be made for the residence time of slurry as it passed through the rig. An "instantaneous" or spot sample taken at time t at the point where hydrolysate came out of the rig (the exit of the condenser) had actually passed through the reactor some time before it was collected. Thus the associated temperatures were not precisely those recorded at the time the sample was taken, but had to be inferred from a knowledge of the reactor dimensions and the measured volumetric flow rate. For a cumulative sample collected over one minute, an average was taken for each thermocouple of the temperatures recorded over that minute. An example of such a calculation is shown below.

Run 51. Configuration number 2



Sample bottle 4. flow rate: 270 ml/min Datalogger on at: 3.21 pm

The first step is to calculate the volume of each stage of the rig. The tubing is 1/4" o.d., 20 S.W.G. (0.036" wall thickness), which has an i.d. of 4.52 mm.

$XSA = (\pi . d^2)/4 = 1.60459 \times 10^{-5}\ m^2$

Volume 1 to 2 = $1.905 \times 1.60459 \times 10^{-5}\ m^3$

= 30.57 ml.

Volume 2 to 3 = 30.57 ml.

Volume 3 to 4 = 8.55 ml.

Volume 4 to 5 = 19.42 ml.

Volume 5 to 6 = 7.75 ml.

Volume 6 to 7 = 282 ml. (measured)

The volumetric flow was 270 ml/min. Thus a sample taken at point 7 at time t will have passed point 1 at time

$$t - (30.57 + 30.57 + 8.55 + 19.42 + 7.75 + 282)/270 = t - 1.40 \text{ minutes}$$

Sample bottle 4 was taken between 3.35 and 3.36 pm, i.e. between minutes 14 and 15 after the Datalogger had been switched on. The average of the temperatures recorded at thermocouple A during this period was 182.1°C. Correcting for the thermocouple:mV-meter calibration gave a corrected temperature of 179°. The other temperatures were calculated similarly.

It should be noted at this point that the temperature recorded by thermocouple C at point 4 is always reported as the temperature at point 3 (e.g., in the tables of results in Appendix 3), and is used as such in the computer programmes to estimate the kinetic parameters. This is because the heating section terminates at point 3, and to include the residence time between points 3 and 4 in the heating calcultaions would give erroneous results. The temperatures at points 3 and 4 can be assumed to be approximately equal as the residence time between these points is small (especially when compared to that in the heating sections or residence time coils) and the insulation is good.

APPENDIX 5

COMPUTER PROGRAM FOR KINETIC PARAMETER ESTIMATION

The programme listed below was used in finding the best values of the kinetic parameters to fit the experimental data. As listed, it is using the values of Thompson and Grethlein (1979) to predict values of C_B which are then compared with the experimentally detemined values of the glucose concentration. The calculation is a numerical integration, using the Runge-Kutte method. The programme uses a subroutine named RUNGK already available in the NAG library on the University of Cambridge computer to perform the integration.

Time is the independent variable, and for each data point the temperature and the values of the kinetic parameters k_1 and k_2 are integrated over the residence time of slurry in the final heating and reactor sections of the rig. The integration is divided into several stages, with temperature a linear function of time in each stage. The subroutine FCN is used by RUNGK to find the values of the first-order differentials of C_A, C_B and T with time. The final predicted value of the glucose concentration for each data point is compared with the actual value, and the difference between the values is noted. The programme also calculates the sum of the differences and the sum of the squares of the differences, to provide an estimate of how well the kinetic parameters being tested are able to predict the experimental data.

```
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION CBREAL(100),TEMP1(100),TIME(100,6),FTEMP(100,6),
     1ACID(100),CA0(100),CB0(100),NSTAGE(100),Y(3)
      COMMON FK,P1,P2,E1,E2,EM,EN,ACID,I
      READ(5,100) N
  100 FORMAT(I3)
      DO 5 I=1,N
      READ(5,110) NSTAGE(I),ACID(I),CA0(I),CB0(I),CBREAL(I)
  110 FORMAT(I3,3F5.2,F6.3)
      NS=NSTAGE(I)
      READ(5,120) TEMP1(I),(FTEMP(I,J),J=1,NS),(TIME(I,J),J=1,NS)
  120 FORMAT(13F6.2)
    5 CONTINUE
      P1=1.22
      P2=3.79
      E1=42500.0
      E2=32700.0
      EM=1.16
      EN=0.69
      R=1.9872
      SIGVAR=0.0
      SIGVSQ=0.0
      DO 20 I=1,N
      Y(1)=CA0(I)
      Y(2)=CB0(I)
      NS=NSTAGE(I)
      TEMP=TEMP1(I)
      DO 10 J=1,NS
      Y(3)=TEMP
      FK=(FTEMP(I,J)-TEMP)/TIME(I,J)
      TT=TIME(I,J)
      CALL RUNGK(Y,TT)
      TEMP=FTEMP(I,J)
   10 CONTINUE
      VAR=CBREAL(I)-Y(2)
      VARSQ=VAR**2
```

```
      WRITE(6,150) I,Y(1),Y(2),CBREAL(I),VAR
  150 FORMAT(3X,I3,3F6.3,F12.8)
      SIGVAR=SIGVAR+VAR
      SIGVSQ=SIGVSQ+VARSQ
   20 CONTINUE
      WRITE(6,160) SIGVAR,SIGVSQ
  160 FORMAT(/,3X,2F12.8)
      STOP
      END
C
      SUBROUTINE RUNGK(Y,TT)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON FK,P1,P2,E1,E2,EM,EN,ACID,I
      DIMENSION W(3,7),Y(3),ACID(100)
      EXTERNAL FCN
      N=3
      TOL=10.**(-3)
      X=0.0
      XEND=TT
      IFAIL=1
      CALL D02BAF(X,XEND,N,Y,TOL,FCN,W,IFAIL)
      RETURN
      END
C
      SUBROUTINE FCN(T,Y,F)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON FK,P1,P2,E1,E2,EM,EN,ACID,I
      DIMENSION Y(3),F(3),ACID(100)
      R=1.9872
      V101=-E1/(R*Y(3))
      V102=-E2/(R*Y(3))
C
      A1=10.0
      A3=ACID(I)
      A2=60.0
      RK1LOG=DLOG(P1)+19.0*DLOG(A1)+EM*DLOG(A3)+V101-DLOG(A2)
```

```
      RK1=DEXP(RK1LOG)
      RK2LOG=DLOG(P2)+14.0*DLOG(A1)+EN*DLOG(A3)+V102-DLOG(A2)
      RK2=DEXP(RK2LOG)
C
      F(1)=-RK1*Y(1)
      F(2)=-RK2*Y(2)+RK1*Y(1)
      F(3)=FK
C
      RETURN
      END
```

APPENDIX 6

SIZE ANALYSIS OF FEEDSTOCKS

The solids used in the hydrolysis experiments (viz, filter paper, newsprint and refuse) had to be ground in a knife mill before being made into slurries, on account of the small diameter of the orifice used to pressurise the reactor and quench the reaction. Samples of each of the ground feedstocks were sent to Spectron Optical Holdings, Limited, of Abingdon, Oxfordshire, for particle size analysis.

These analyses were carried out using a CILAS 715 Laser Granulometer, which operates by measuring the diffraction of a coherent light beam by the grains of a powder sample which are held in suspension in a suitable liquid medium. The results are shown in Table A.6.1. As may be seen, the size analyses for the three feedstocks are quite similar, and thus variation in particle size was not considered to be a factor in the experiments.

Table A.6.1

Particle size analysis of cellulosic feedstocks

	Cumulative Percentage Undersize		
microns	filter paper	newsprint	refuse
1	000.7	000.4	000.7
6	004.7	004.2	005.8
12	006.1	008.7	010.3
16	010.6	012.2	015.8
24	022.4	018.5	025.5
32	033.3	024.0	032.6
48	050.1	042.9	054.5
64	052.6	045.6	054.5
96	064.7	059.9	071.9
128	082.3	079.9	085.9
192	100.0	100.0	100.0

APPENDIX 7

CELLULOSE CONTENT OF FEEDSTOCKS

The cellulose content of the feedstocks used in the hydrolysis experiments was determined by the quantitative saccharification method described in Appendix A.1.2. The results for filter paper, newsprint and refuse are shown below, in Tables A.7.1, A.7.2 and A.7.3.

Table A.7.1

Cellulose content of filter paper feedstock

sample no	sample taken (g)	cellulose content (wt %)
1	0.3330	97.3
2	0.3494	96.4
3	0.3088	96.9
4	0.3284	98.1
5	0.3010	96.0
6	0.3198	95.5
	average:	96.7

Table A.7.2

Cellulose content of newsprint feedstock

sample no	sample taken (g)	cellulose content (wt %)
1	0,2274	53,5
2	0,2773	51,9
3	0,4154	51,7
4	0,4275	52,1
5	0,4149	51,8
6	0,4012	53,9
7	0,3435	52,0
8	0,3642	49,6
9	0,3322	51,2
10	0,3721	51,0
	average:	51,9

Correcting for the value found for filter paper gives

cellulose content of newsprint = 51,9/0,967

= 53,7%

Table A.7.3

Cellulose content of refuse feedstock

sample no	sample taken (g)	cellulose content (wt %)
1	0.5143	43.0
2	0.3966	44.1
3	0.4348	42.8
4	0.4235	42.0
5	0.3403	43.3
6	0.3282	41.9
7	0.3195	42.5
8	0.3132	44.3
	average:	43.0

Correcting for the value found for filter paper gives

cellulose content of refuse sample = 43.0/0.967

= 44.4%

ADDENDUM

CORRECTIONS TO THE RESULTS

Introduction

Subsequent to the submission of this thesis to the external examiners, further experiments were conducted which revealed an error in the results of the newsprint and refuse hydrolysis tests, and the glucose decomposition tests. As a result of interference from acid corrosion products in the hydrolysate, the readings produced by the Glucose Analyser were too high. Corrected results were presented at the oral examination, and are presented again here, so that the information conveyed by this thesis may be as accurate as possible.

Details of the experiments undertaken

Further experiments were carried out because the author was dissatisfied with the results of the newsprint and refuse hydrolysis tests (presented in Chapter 5). As was pointed out on page 139, problems were experienced with the Glucose Analyser when runs were first made with newsprint as feed. The situation was much improved after neutralisation of the hydrolysate to a pH of 6, and all subsequent hydrolysate samples were neutralised prior to glucose analysis.

The glucose readings obtained from the neutralised samples, however, were still rather high, corresponding to very high conversions of cellulose to glucose, and the suspicion arose that there were other compounds in the hydrolysate interfering with the glucose analysis that had not been accounted for. Particularly disturbing were the values of the kinetic parameters that were found to give the best fit to the data. These appeared to indicate that the rate of decomposition of glucose was

independent of the acid concentration (n=0.0), a fact not borne out by the study of the glucose decomposition kinetics (n=0.59, page 153).

Accordingly, three runs were carried out with only water and acid in the feed. The concentrations of sulphuric acid used were 0.5, 1.0 and 1.5%, as in the hydrolysis experiments, and the temperature was varied from (approximately) 210° to 240°C. Product smples were collected in the usual way, and neutralised and injected into the Glucose Analyser - as if a glucose analysis was being carried out. It was found that in each case an "apparent" glucose reading was measured, which increased with increasing acid concentration and temperature. For each acid concentration, a linear relationship was found between the apparent glucose reading and the maximum temperature in the rig at the time the sample was taken. A plot of these results is shown in Figure A.1.

These results show that without any cellulosic material or glucose in the feed, a positive reading for glucose was obtained on the Glucose Analyser. It was deduced that the phenomenon could only be attributed to the presence of acid corrosion products in the samples, ie the products of the reaction of hot dilute sulphuric acid with metals in the stainless steel tubing. (The presence of metallic ions in the samples was indicated by the green colour of the solutions). How this interference came about, and why it should only have been a problem in the later stages of the work, and not during the filter paper experiments, remained to be established.

Interpretation of the experimental results

As outlined in Appendix A.1.1.2, the Glucose Analyser relies on the reaction of glucose with an immobilised glucose oxidase enzyme to produce hydrogen peroxide, which diffuses to a platinum electrode. At the probe anode, the hydrogen peroxide is oxidised electrochemically, giving rise to the probe signal current. The probe is protected against other oxidisable substances by a very thin layer of cellulose acetate; but this layer is known to be permeable to hydrogen peroxide, hydrazine, hydrogen sulphide

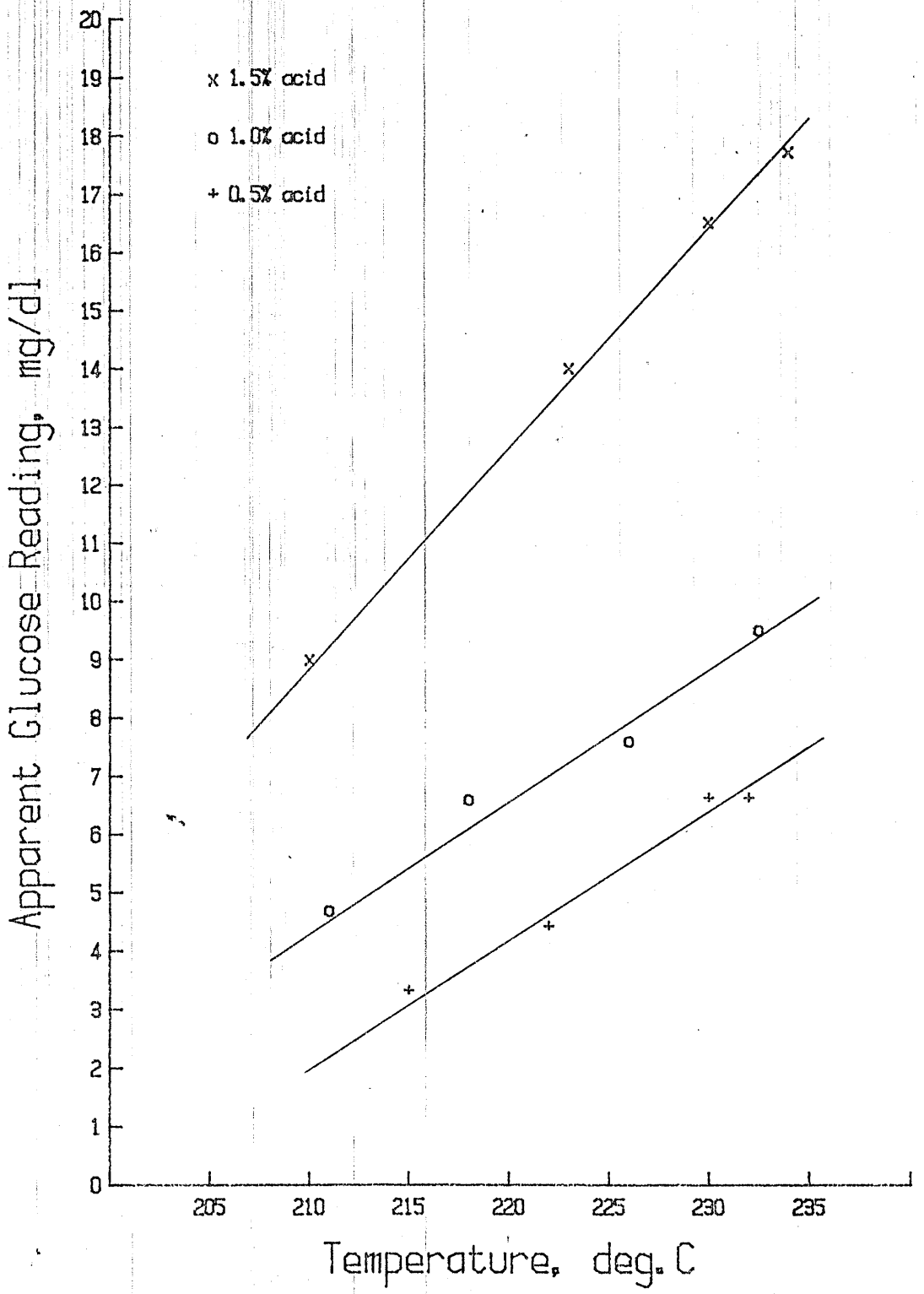


Figure A.1. Glucose interference from acid corrosion products.

and mercaptans. [1]

It is quite possible, therefore, to imagine that small metal ions might also be able to permeate the membrane, and diffuse to the anode, to be oxidised to higher oxidation states. Iron, chromium and nickel (the chief constituents of 316S stainless steel) all have more than one oxidation state, and could all possibly interfere with the glucose reading. In order to determine whether this was in fact the case, a dilute solution of ferrous sulphate was made up, containing 0.1 g per litre of ferrous ion. When injected into the Glucose Analyser, this solution gave a reading of 5 mg/dl. A 1% solution of sodium sulphate, on the other hand, gave a zero reading on the Glucose Analyser. This evidence suggested that the presence of acid corrosion products did indeed lead to erroneously high glucose readings being obtained from hydrolysate samples analysed using the YSI Industrial Analyser.

A check was also made on whether the interference from these ions persisted in the presence of glucose, by adding a measured quantity of anhydrous glucose to a sample of dilute sulphuric acid which had been passed through the rig at high temperature, to make up a solution containing 100 mg/dl of glucose. The original (spurious) reading of the sample was 7 mg/dl; after the addition of the glucose it was 107 mg/dl. This showed that the interference was (a) additive, and (b) still present when the total glucose reading on the Analyser was of the order of 100 mg/dl. (In the refuse and newsprint hydrolysis tests, all the sample readings were lower than 100 mg/dl). The evidence that interference by acid corrosion products leads to erroneously high glucose readings was therefore taken to be conclusive.

In order to understand why this problem should only have been observed when the runs with newsprint as cellulosic feedstock were begun, the nature of corrosion resistance in stainless steels was examined. It appears that stainless steels owe their unusual corrosion resistance to a condition known as "passivity", which results from the presence of thin

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[1] Dextrose specification sheet, YSI Co. Inc., Scientific Division, Yellow Springs, Ohio, 1982.

oxide films called "passive films". Under favourable conditions, such films are protective; unfavourable conditions destroy the films and leave the surface in the "active" state, with corrosion resistance only slightly superior to that of ordinary iron or steel. [2]

Conditions of so-called "borderline passivity" are also known, in which small changes in the environment will change the passive to the active state or vice versa. The results are unpredictable variations in resistance to general corrosion. Dilute sulphuric acid solutions, especially when hot, are apparently notorious in this respect! The conditions required to preserve passivity are the presence of air or small amounts of oxidising agents (such as nitric acid or copper sulphate) while the presence of reducing agents destroys passivity under conditions that might otherwise be satisfactory. Passivity, once destroyed, may be restored by treatment with oxidising solutions or by exposing the surface to air.

It is surmised, therefore, that the passive film was destroyed during the initial series of tests with newsprint (runs 71 to 82, which were lost on account of problems with the Glucose Analyser) and that corrosion continued to take place throughout the remainder of the experiments. This would have to be put down to the presence of some reducing agent in newsprint which is not present in filter paper, which is 100% cellulose. It could be the carbon black in the newspaper ink (which is known to undergo oxidation in preference to reduction) or to some compound in the filler material which is used in the manufacture of the paper. In any event, this hypothesis may be tested by repeating some of the filter paper experiments, to determine whether the results are unusually high; or by restoring the passive film (by blowing air through the rig for example) and carrying out more experiments with newsprint, adding small amounts of copper sulphate to preserve passivity, to see whether the glucose readings are lower than those previously determined.

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[2] "The selection of stainless steels for corrosive service in chemical processing equipment", Metals Handbook, Volume 1, pp 564-76, American Society for Metals, Metals Park, Ohio, 1961.

As a result of this investigation, the use of materials of construction in the rig that are more resistant to acid corrosion (such as Carpenter 20-Cb3, or PTFE-lined stainless steel) becomes even more urgent than was previously stated (page 163).

Corrections to the previous results

Knowing that the presence of acid corrosion products leads to erroneously high glucose readings being obtained on the Glucose Analyser, an attempt has been made to correct the previous results (of the newsprint and refuse hydrolysis tests, and the glucose decomposition tests) by allowing for the interference that would have resulted from the presence of these ions. This was done by considering as blanks the samples of water and acid only that were passed through the rig and "analysed" for glucose, and using the curves of apparent glucose reading versus maximum temperature for the three acid concentrations (Figure A.1) to predict the interference that would be expected under the conditions of each of the previously determined sample points. This interference was then subtracted from the previous reading (of glucose concentration), and new values of glucose conversion were calculated.

As a result of these manipulations, corrected versions of the tables of raw data were drawn up (Tables A.3.2, A.3.3, and A.3.4) and appear at the end of this text. Corrected versions of the summary tables (Tables 5.3, 5.4 and 5.6) are also presented, together with revised versions of the plots of these results (Figures 5.2, 5.3 and 5.4). The obvious effect on the hydrolysis results of making these corrections is that the values of cellulose conversion obtained are lower, the more so at the higher temperatures, where the interference from acid corrosion products is greater. The curves of cellulose conversion versus temperature (for example, in the revised Figure 5.3 for the newsprint hydrolysis results) therefore have a more gentle slope, and are more obviously approaching a maximum. The increase of glucose yield with increasing temperature and acid concentration may still be seen, though at higher temperatures and longer residence times the results obtained with the lower catalyst

concentration overtake those obtained at the higher acid level, indicating once again that the conversion goes through a maximum. The revised data shows that the highest value of cellulose conversion obtained during the newsprint hydrolysis tests was 63.4% (1.0% acid, 231°C, configuration number 5), while the highest value obtained from the hydrolysis of refuse was 52.6%, when using 1.0% acid at 234°C and with configuration number 3.

The effect of making these changes is perhaps most marked, however, in the new values of the kinetic parameters that were derived to fit the revised data. This is especially so in the case of refuse, for, after allowing for an initial glucose content C_{B0} of 0.1, corresponding to an amorphous cellulose content C_{A0} of 0.9, the kinetic parameters derived by Thompson and Grethlein (1979) were found to fit the data very well. So too did the parameters derived previously from the filter paper experiments. The best fit was found to be given by the following values (cf Table 5.2)

$P_1 = 1.22 \times 10^{19}$ min^{-1}
$m = 1.16$
$E_1 = 42\,460$ cal/mol
$P_2 = 3.79 \times 10^{14}$ min^{-1}
$n = 0.69$
$E_2 = 32\,800$ cal/mol

and the comparison between the predicted and actual values is shown below, in a revised Table 5.5.

The kinetic parameters derived to fit the revised newsprint data were also very reasonable. The published parameters of Saeman (1945), Fagan et al (1971), and Thompson and Grethlein (1979) all fitted the revised data much better than they had done the original data: the best fit (also assuming C_{B0}=0.1) was found to be given by the values

$P_1 = 1.52 \times 10^{19}$ min^{-1}
$m = 1.06$

E_1 = 42 400 cal/mol

P_2 = 3.49 x 10^{14} min^{-1}

n = 0.59

E_2 = 33 000 cal/mol

Using these values, the sum of the deviations was found to be 0.285, and the sum of squared deviations 0.160.

The corrections made to the glucose decomposition figures increased the values of glucose conversion, as lower glucose concentrations in the product indicated that more glucose was decomposed during the reaction than was previously thought. New kinetic parameters were derived to fit the revised data: the best correlation was obtained with the values

P_2 = 3.74 x 10^{14} min^{-1}

n = 0.69

E_2 = 32 000 cal/mol

The sum of the deviations between predicted and actual values was -0.020, and the sum of the squared deviations 0.526. This is still not a very good fit, and the original comments made on page 153 are still thought to hold good.

Revised conclusions and recommendations for further work

In the light of the data presented above, some of the conclusions reached in Chapter 7 need to be revised. In particular, the yields of glucose obtained from the hydrolysis of newsprint and air classified lights are now known to be lower than originally reported, because of interference from acid corrosion products with the readings on the Glucose Analyser. However, after correcting the results to take into account the effect of this interference, the kinetic parameters found agree well with those obtained by previous investigators. The parameter values which were found to describe the hydrolysis of refuse are almost identical with those

of Thompson and Grethlein (1979), and are very similar to the values obtained from the filter paper work. The values obtained from the newsprint experiments are not much different. The strange values derived previously from the newsprint and refuse results were shown to be invalid.

As the original kinetic parameter values for refuse are incorrect, however, the calculated values of maximum glucose yield and optimum isothermal reaction time listed in Table 6.1 (page 170) are also wrong, thereby invalidating the mass balance in Chapter 6. The revised data indicates that the yield of glucose from air classified lights at 220°C, 1.0% acid and a reaction time of 35 seconds would be much lower than 61.7%. A value of 40% would be more realistic, resulting in a lower ethanol yield from the plant, and more uneconomical operation. Under these circumstances, the cost of landfilling or the selling price of ethanol (or both) would have to rise significantly for the acid hydrolysis route to become a viable alternative method of refuse disposal. Alternatively, fermentation technology would have to be improved to allow higher ethanol yields than 6% vol/vol to be produced, and thereby reduce the costs of distilling the extra water.

Finally, as a result of the findings that have been made about the effect of acid corrosion products on the Glucose Analyser reading, it will be necessary during future work with the rig to keep this factor in mind. Adding an oxidising agent such as copper sulphate to the slurry feed might be all that is required to prevent corrosion, once the passive layer has been restored (this could be investigated by checking the glucose analysis by an alternative method, or by deionising a sample of hydrolysate and comparing the glucose readings before and after deionisation). But if corrosion may not be prevented in this way, then alternative materials of construction would need to be found. Carrying out the glucose analysis by high performance liquid chromatography would circumvent the (analytical) problem, as the concentration of sugars is measured by refractive index (see Appendix 1), but the method would only be useful if experiments were conducted at higher slurry concentrations. An added advantage, however, would be that the concentration of other sugars in the hydrolysates could be determined in this way.

Table A.3.2

Detailed results of newsprint hydrolysis tests*

	FEED				TEMPERATURE						RESIDENCE TIME (seconds)						HYDROLYSATE			
RUN NO	ACID CONC %	SLURRY CONC %	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	RES CELL %	GLUC* CONC mg/dl	GLUC* CONV %	DECOMP* PROD %
86	1.48	0.209	285	1	169	199	195	194	-	-	6.44	6.44	2.74	0.98	--	--	85.6	35.7	28.6	**
86	1.48	0.209	280	1	174	208	216	214	-	-	6.55	6.55	2.79	0.99	--	--	37.6	47.7	38.3	24.1
86	1.48	0.209	270	1	179	214	227	226	-	-	6.79	6.79	2.90	1.03	--	--	11.8	62.8	50.4	37.8
86	1.48	0.209	265	1	183	218	236	235	-	-	6.92	6.92	2.95	1.05	--	--	8.8	71.7	57.5	33.7
87(a)	1.00	0.141	270	1	169	199	196	194	-	-	6.79	6.79	2.90	1.03	--	--	72.1	20.7	24.6	3.3
87(a)	1.00	0.141	275	1	171	207	217	216	-	-	6.67	6.67	2.84	1.01	--	--	52.2	29.8	35.4	12.4
87(a)	1.00	0.141	265	1	174	209	226	226	-	-	6.92	6.92	2.95	1.05	--	--	44.2	36.0	42.8	13.0
87(a)	1.00	0.141	255	1	183	218	235	236	-	-	7.19	7.19	3.07	1.09	--	--	15.3	47.9	56.9	27.8
87(b)	0.50	0.070	280	1	173	210	215	214	-	-	6.55	6.55	2.79	0.99	--	--	59.7	10.1	24.2	16.1
87(b)	0.50	0.070	280	1	176	214	224	224	-	-	6.55	6.55	2.79	0.99	--	--	47.0	11.4	27.3	25.7
87(b)	0.50	0.070	255	1	185	222	236	236	-	-	7.19	7.19	3.07	1.09	--	--	31.2	16.4	39.3	29.5
88(a)	1.47	0.214	300	5	175	201	199	192	187	183	6.11	6.11	9.47	3.88	3.88	1.55	73.9	37.7	29.5	**
88(a)	1.47	0.214	280	5	177	212	215	215	213	209	6.55	6.55	10.15	4.16	4.16	1.66	49.8	56.9	44.6	5.6
88(a)	1.47	0.214	275	5	184	219	223	223	223	221	6.67	6.67	10.34	4.24	4.24	1.69	12.3	67.6	52.9	34.8
88(a)	1.47	0.214	255	5	201	230	230	231	231	231	7.19	7.19	11.15	4.57	4.57	1.82	7.8	73.0	57.2	35.0
88(b)	0.99	0.137	260	5	193	218	217	217	217	217	7.05	7.05	10.93	4.48	4.48	1.79	--	38.6	47.2	--
88(b)	0.99	0.137	245	5	195	225	226	226	226	226	7.49	7.49	11.61	4.76	4.76	1.90	--	49.6	60.7	--
88(b)	0.99	0.137	245	5	203	231	231	231	231	231	7.49	7.49	11.61	4.76	4.76	1.90	--	51.8	63.4	--

Table A.3.2 (continued)
Detailed results of newsprint hydrolysis tests*

	FEED																	HYDROLYSATE		
					TEMPERATURE						RESIDENCE TIME (seconds)									
RUN NO	ACID CONC %	SLURRY CONC %	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	RES CELL %	GLUC* CONC mg/dl	GLUC* CONV %	DECOMP* PROD %
88(c)	0.49	0.068	260	5	190	218	217	217	217	218	7.05	7.05	10.93	4.48	4.48	1.79	--	14.8	36.5	--
88(c)	0.49	0.068	250	5	200	224	223	223	223	223	7.34	7.34	11.37	4.66	4.66	1.86	--	17.8	43.9	--
88(c)	0.49	0.068	250	5	201	228	227	227	227	227	7.34	7.34	11.37	4.66	4.66	1.86	--	21.1	52.0	--
89(a)	1.47	0.211	290	3	169	198	194	189	183	-	6.33	6.33	5.79	4.02	1.60	--	--	37.3	29.6	--
89(a)	1.47	0.211	280	3	174	209	214	208	202	-	6.55	6.55	5.99	4.16	1.66	--	--	52.3	41.5	--
89(a)	1.47	0.211	280	3	177	212	226	220	213	-	6.55	6.55	5.99	4.16	1.66	--	--	67.0	53.2	--
89(a)	1.47	0.211	280	3	179	214	234	228	222	-	6.55	6.55	5.99	4.16	1.66	--	--	70.0	55.6	--
89(b)	1.00	0.139	290	3	173	208	216	211	206	-	6.33	6.33	5.79	4.02	1.60	--	--	37.0	44.6	--
89(b)	1.00	0.139	285	3	177	212	224	218	213	-	6.44	6.44	5.89	4.09	1.63	--	--	43.5	52.5	--
89(b)	1.00	0.139	270	3	182	217	235	233	228	-	6.79	6.79	6.22	4.32	1.72	--	--	50.4	60.8	--
90	0.50	0.076	292	3	176	210	215	210	205	-	6.28	6.28	5.74	3.99	1.59	--	--	15.5	34.2	--
90	0.50	0.076	280	3	183	215	226	221	216	-	6.55	6.55	5.99	4.16	1.66	--	--	16.4	36.2	--
90	0.50	0.076	265	3	190	218	234	234	231	-	6.92	6.92	6.33	4.40	1.75	--	--	17.9	39.5	--

Table A.3.3

Detailed results of refuse hydrolysis tests*

	FEED																HYDROLYSATE		
					TEMPERATURE						RESIDENCE TIME (seconds)								
RUN NO	ACID CONC %	SLURRY CONC %	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	RES SOLID %	GLUC CONC* mg/dl	GLUC CONV* %
93	1.46	0.200	313	1	170	205	226	223	-	-	5.86	5.86	2.50	0.89	--	--	45.3	35.2	35.7
93	1.46	0.200	313	1	173	211	230	227	-	-	5.86	5.86	2.50	0.89	--	--	38.5	38.8	39.3
93	1.46	0.200	287	1	175	215	233	230	-	-	6.39	6.39	2.72	0.97	--	--	32.8	42.7	43.3
94	0.99	0.131	295	1	170	200	219	218	-	-	6.22	6.22	2.65	0.94	--	--	52.3	17.6	27.2
94	0.99	0.131	288	1	186	212	227	227	-	-	6.37	6.37	2.71	0.97	--	--	44.7	27.6	42.7
94	0.99	0.131	255	1	188	217	234	234	-	-	7.19	7.19	3.07	1.09	--	--	37.3	34.0	52.6
95	0.99	0.131	295	3	175	207	221	222	219	-	6.22	6.22	5.69	3.95	1.58	--	49.1	25.0	38.7
95	0.99	0.131	275	3	197	219	228	229	228	-	6.67	6.67	6.10	4.24	1.69	--	39.8	31.4	48.6
95	0.99	0.131	268	3	198	225	232	233	232	-	6.84	6.84	6.26	4.35	1.73	--	33.8	33.9	52.5
96	1.43	0.199	260	3	187	211	219	219	217	-	7.05	7.05	6.45	4.48	1.79	--	48.2	41.7	42.5
96	1.43	0.199	260	3	199	216	226	226	226	-	7.05	7.05	6.45	4.48	1.79	--	37.9	44.2	45.0
96	1.43	0.199	250	3	199	228	231	232	232	-	7.34	7.34	6.71	4.66	1.86	--	29.7	44.3	45.1
97a	1.43	0.199	280	5	190	214	217	217	217	215	6.55	6.55	10.15	4.16	4.16	1.66	52.0	37.5	38.2
97a	1.43	0.199	255	5	202	226	226	226	227	227	7.19	7.19	11.15	4.57	4.57	1.82	40.2	45.5	46.4
97a	1.43	0.199	235	5	217	230	230	230	230	230	7.81	7.81	12.10	4.96	4.96	1.98	29.8	44.9	45.7
97b	0.95	0.130	272	5	195	209	209	209	209	207	6.74	6.74	10.45	4.28	4.28	1.71	62.5	21.7	33.8
97b	0.95	0.130	277	5	190	216	216	216	216	216	6.62	6.62	10.26	4.21	4.21	1.68	57.2	23.6	36.8
97b	0.95	0.130	250	5	200	223	223	223	224	224	7.34	7.34	11.37	4.66	4.66	1.86	47.5	28.7	44.8
97b	0.95	0.130	265	5	206	228	228	227	228	228	6.92	6.92	10.73	4.40	4.40	1.75	39.0	29.8	46.5

Table A.3.4

Detailed results of glucose decomposition tests*

	FEED																PRODUCT		
					TEMPERATURE						RESIDENCE TIME (seconds)								
RUN NO	ACID CONC %	GLUC CONC mg/dl	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	GLUC* CONC mg/dl	GLUC* DECOMP %	RES* GLUC %
83(a)	1.47	297	230	3	191	193	187	179	172	-	7.97	7.97	7.30	5.07	2.02	--	251	15.5	84.5
83(a)	1.47	297	245	3	197	207	210	193	186	-	7.49	7.49	6.85	4.76	1.90	--	213	28.3	71.7
83(a)	1.47	297	240	3	198	220	217	210	203	-	7.64	7.64	6.99	4.86	1.94	--	146	50.8	49.2
83(a)	1.47	297	225	3	206	224	229	226	218	-	8.15	8.15	7.46	5.18	2.07	--	93	68.7	31.3
83(a)	1.47	297	215	3	215	228	237	236	235	-	8.53	8.53	7.81	5.42	2.16	--	58	80.5	19.5
83(b)	1.01	209	250	3	197	206	202	196	190	-	7.34	7.34	6.71	4.66	1.86	--	147	29.7	70.3
83(b)	1.01	209	245	3	201	221	221	211	205	-	7.49	7.49	6.85	4.76	1.90	--	106	49.3	50.7
83(b)	1.01	209	235	3	209	227	226	223	216	-	7.81	7.81	7.14	4.96	1.98	--	87	58.4	41.6
83(b)	1.01	209	215	3	217	232	235	234	233	-	8.53	8.53	7.81	5.42	2.16	--	58	72.2	27.8
83(c)	0.50	101	250	3	195	202	198	192	187	-	7.34	7.34	6.71	4.66	1.86	--	81	19.8	80.2
83(c)	0.50	101	215	3	194	220	216	208	202	-	8.53	8.53	7.81	5.42	2.16	--	64	36.6	63.4
83(c)	0.50	101	230	3	200	226	226	224	216	-	7.97	7.97	7.30	5.07	2.02	--	50	50.5	49.5
83(c)	0.50	101	235	3	213	232	235	234	234	-	7.81	7.81	7.14	4.96	1.98	--	32	68.3	31.7
84(a)	0.49	401.5	230	5	188	206	201	190	185	180	7.97	7.97	12.37	5.07	5.07	2.02	351	12.6	87.4
84(a)	0.49	401.5	260	5	189	215	214	206	201	194	7.05	7.05	10.93	4.48	4.48	1.79	312	22.3	77.7
84(a)	0.49	401.5	250	5	197	225	226	226	226	223	7.34	7.34	11.37	4.66	4.66	1.86	219	45.4	54.6
84(a)	0.49	401.5	225	5	206	233	233	233	233	233	8.15	8.15	12.64	5.18	5.18	2.07	149	62.9	37.1
84(b)	1.45	398.5	245	5	186	189	187	179	175	171	7.49	7.49	11.61	4.76	4.76	1.90	339	14.9	85.1
84(b)	1.45	398.5	230	5	189	203	199	189	183	178	7.97	7.97	12.37	5.07	5.07	2.02	304	23.7	76.3
84(b)	1.45	398.5	245	5	192	217	215	210	204	198	7.49	7.49	11.61	4.76	4.76	1.90	227	43.0	57.0
84(b)	1.45	398.5	230	5	206	227	227	227	226	223	7.97	7.97	12.37	5.07	5.07	2.02	138	65.4	34.6
84(b)	1.45	398.5	220	5	213	235	235	235	235	235	8.34	8.34	12.92	5.30	5.30	2.11	103	74.1	25.9

Table A.3.4 (continued)

Detailed results of glucose decomposition tests*

	FEED																PRODUCT		
					TEMPERATURE						RESIDENCE TIME (seconds)								
RUN NO	ACID CONC %	GLUC CONC mg/dl	FLOW RATE ml/ min	CON FIG NO	A	B	C	D	E	F	1	2	3	4	5	6	GLUC* CONC mg/dl	GLUC* DECOMP %	RES* GLUC %
84(c)	0.95	261	235	5	190	197	195	185	181	177	7.81	7.81	12.10	4.96	4.96	1.98	222	14.9	85.1
84(c)	0.95	261	240	5	198	216	216	214	208	202	7.64	7.64	11.85	4.86	4.86	1.94	164	37.2	62.8
84(c)	0.95	261	232	5	204	226	225	225	225	222	7.91	7.91	12.26	5.02	5.02	2.00	113	56.7	43.3
84(c)	0.95	261	225	5	213	234	233	233	233	233	8.15	8.15	12.64	5.18	5.18	2.07	73	72.0	28.0
85(a)	1.46	302	252	1	182	187	182	180	-	-	7.28	7.28	3.10	1.10	--	--	264	12.6	87.4
85(a)	1.46	302	248	1	189	206	201	199	-	-	7.40	7.40	3.15	1.12	--	--	229	24.2	75.8
85(a)	1.46	302	238	1	195	223	220	219	-	-	7.71	7.71	3.28	1.17	--	--	138	54.3	45.7
85(a)	1.46	302	230	1	200	226	230	230	-	-	7.97	7.97	3.40	1.21	--	--	106	64.9	35.1
85(a)	1.46	302	230	1	207	230	237	237	-	-	7.97	7.97	3.40	1.21	--	--	68	77.5	22.5
85(b)	0.96	199	245	1	187	202	199	198	-	-	7.49	7.49	3.19	1.14	--	--	160	19.6	80.4
85(b)	0.96	199	245	1	193	223	220	219	-	-	7.49	7.49	3.19	1.14	--	--	114	42.7	57.3
85(b)	0.96	199	245	1	199	226	228	228	-	-	7.49	7.49	3.19	1.14	--	--	90	54.8	45.2
85(b)	0.96	199	220	1	205	228	234	235	-	-	8.34	8.34	3.55	1.27	--	--	70	64.8	35.2
85(c)	0.48	98	247	1	191	202	199	198	-	-	7.43	7.43	3.17	1.13	--	--	82	16.3	83.7
85(c)	0.48	98	255	1	189	218	215	213	-	-	7.19	7.19	3.07	1.09	--	--	68	30.6	69.4
85(c)	0.48	98	240	1	199	223	226	227	-	-	7.64	7.64	3.26	1.16	--	--	52	46.9	53.1
85(c)	0.48	98	233	1	203	224	234	235	-	-	7.87	7.87	3.36	3.97	--	--	40	59.2	40.8

Table 5.3

Summary of newsprint hydrolysis results*

run no	con fig no	acid conc %	temperatures A	B	C	D	E	F	cell conv* %
86	1	1.5	174	208	216	214	---	---	38.3
87a	1	1.0	171	207	217	216	---	---	35.4
87b	1	0.5	173	210	215	214	---	---	24.2
89a	3	1.5	174	209	214	208	202	---	41.5
89b	3	1.0	173	208	216	211	206	---	44.6
90	3	0.5	176	210	215	210	205	---	34.2
88a	5	1.5	177	212	215	215	213	209	44.6
88b	5	1.0	193	218	217	217	217	217	47.2
88c	5	0.5	190	218	217	217	217	218	36.5
86	1	1.5	179	214	227	226	---	---	50.4
87a	1	1.0	174	209	226	226	---	---	42.8
87b	1	0.5	176	214	224	224	---	---	27.3
89a	3	1.5	177	212	226	220	213	---	53.2
89b	3	1.0	177	212	224	218	213	---	52.5
90	3	0.5	183	215	226	221	216	---	36.2
88a	5	1.5	184	219	223	223	223	221	52.9
88b	5	1.0	195	225	226	226	226	226	60.7
88c	5	0.5	200	224	223	223	223	223	43.9
86	1	1.5	183	218	236	235	---	---	57.5
87a	1	1.0	183	218	235	236	---	---	56.9
87b	1	0.5	185	222	236	236	---	---	39.3
89a	3	1.5	179	214	234	228	222	---	55.6
89b	3	1.0	182	217	235	233	228	---	60.8
90	3	0.5	190	218	234	234	231	---	39.5
88a	5	1.5	201	230	230	231	231	231	57.2
88b	5	1.0	203	231	231	231	231	231	63.4
88c	5	0.5	201	228	227	227	227	227	52.0

Table 5.4

Summary of refuse hydrolysis results*

run no	con fig no	acid conc %	temperatures A	B	C	D	E	F	cell conv* %
93	1	1.5	170	205	226	223	---	---	35.7
94	1	1.0	170	200	219	218	---	---	27.2
96	3	1.5	187	211	219	219	217	---	42.5
95	3	1.0	175	207	221	222	219	---	38.7
97a	5	1.5	190	214	217	217	217	215	38.2
97b	5	1.0	195	209	209	209	209	207	33.8
93	1	1.5	173	211	230	227	---	---	39.3
94	1	1.0	186	212	227	227	---	---	42.7
96	3	1.5	199	216	226	226	226	---	45.0
95	3	1.0	197	219	228	229	228	---	48.6
97a	5	1.5	202	226	226	226	227	227	46.4
97b	5	1.0	190	216	216	216	216	216	36.8
93	1	1.5	175	215	233	230	---	---	43.3
94	1	1.0	188	217	234	234	---	---	52.6
96	3	1.5	199	228	231	232	232	---	45.1
95	3	1.0	198	225	232	233	232	---	52.5
97a	5	1.5	217	230	230	230	230	230	45.7
97b	5	1.0	200	223	223	223	224	224	44.8
97b	5	1.0	206	228	228	227	228	228	46.5

Table 5.5

Refuse hydrolysis - residuals for the glucose yield model*

data point	C_B(est)	C_B(real)	residual
1	0.232	0.272	0.03998
2	0.326	0.427	0.10141
3	0.453	0.526	0.07338
4	0.376	0.387	0.01067
5	0.487	0.486	-0.00064
6	0.510	0.525	0.01477
7	0.377	0.357	-0.02046
8	0.452	0.393	-0.05899
9	0.514	0.433	-0.08060
10	0.434	0.425	-0.00906
11	0.521	0.450	-0.07104
12	0.493	0.451	-0.04164
13	0.460	0.382	-0.07781
14	0.469	0.464	-0.00451
15	0.342	0.457	0.11532
16	0.275	0.338	0.06342
17	0.368	0.368	-0.00041
18	0.474	0.448	-0.02557
19	0.485	0.465	-0.01978
SUM OF RESIDUALS			0.00844
SUM OF SQUARES OF RESIDUALS			0.05930

Table 5.6

Summary of glucose decomposition results*

run no	con fig no	acid conc %	temperatures A	B	C	D	E	F	gluc conv* %
85a	1	1.5	182	187	182	180	---	---	12.6
83a	3	1.5	191	193	187	179	172	---	15.5
84b	5	1.5	186	189	187	179	175	171	14.9
85a	1	1.5	189	206	201	199	---	---	24.2
85b	1	1.0	187	202	199	198	---	---	19.6
85c	1	0.5	191	202	199	198	---	---	16.3
83a	3	1.5	197	207	210	193	186	---	28.3
83b	3	1.0	197	206	202	196	190	---	29.7
83c	3	0.5	195	202	198	192	187	---	19.8
84b	5	1.5	189	203	199	189	183	178	23.7
84c	5	1.0	190	197	195	185	181	177	14.9
84a	5	0.5	188	206	201	190	185	180	12.6
85a	1	1.5	195	223	220	219	---	---	54.3
85b	1	1.0	193	223	220	219	---	---	42.7
85c	1	0.5	189	218	215	213	---	---	30.6
83a	3	1.5	198	220	217	210	203	---	54.8
83b	3	1.0	201	221	221	211	205	---	49.3
83c	3	0.5	194	220	216	208	202	---	36.6
84b	5	1.5	192	217	215	210	204	198	43.0
84c	5	1.0	198	216	216	214	208	202	37.2
84a	5	0.5	189	215	214	206	201	194	22.3
85a	1	1.5	200	226	230	230	---	---	64.9
85b	1	1.0	199	226	228	228	---	---	54.8
85c	1	0.5	199	223	226	227	---	---	46.9
83a	3	1.5	206	224	229	226	218	---	68.7
83b	3	1.0	209	227	226	223	216	---	58.4
83c	3	0.5	200	226	226	224	216	---	50.5
84b	5	1.5	206	227	227	227	226	223	65.4
84c	5	1.0	204	226	225	225	225	222	56.7
84a	5	0.5	197	225	226	226	226	223	45.4
85a	1	1.5	207	230	237	237	---	---	77.5
85b	1	1.0	205	228	234	235	---	---	64.8
85c	1	0.5	203	224	234	235	---	---	59.2
83a	3	1.5	215	228	237	236	235	---	80.5
83b	3	1.0	217	232	235	234	233	---	72.2
83c	3	0.5	213	232	235	234	234	---	68.3
84b	5	1.5	213	235	235	235	235	235	74.1
84c	5	1.0	213	234	233	233	233	233	72.0
84a	5	0.5	206	233	233	233	233	233	62.9

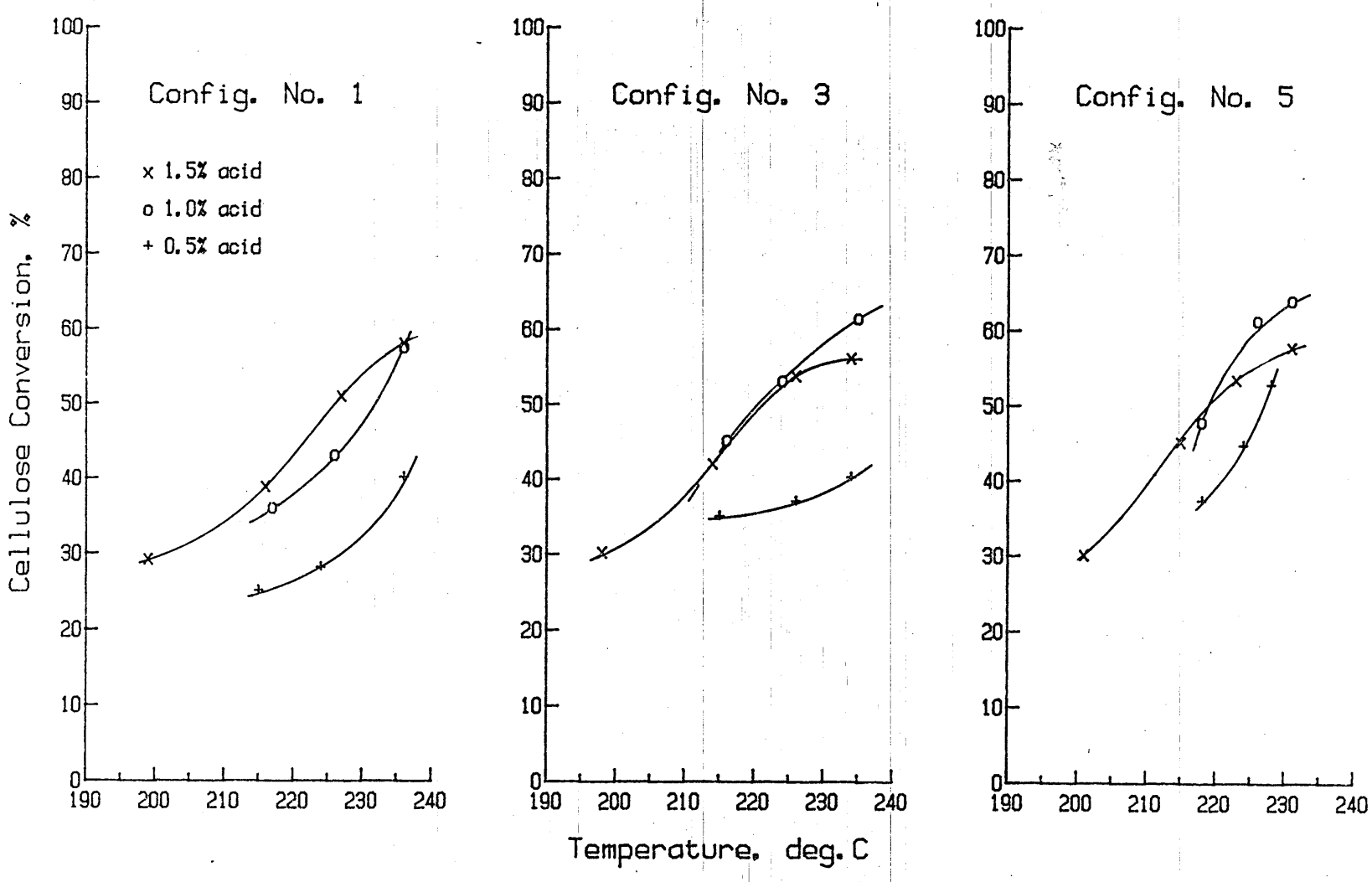

Figure 5.2 (revised). Variation of glucose yield for newsprint hydrolysis.

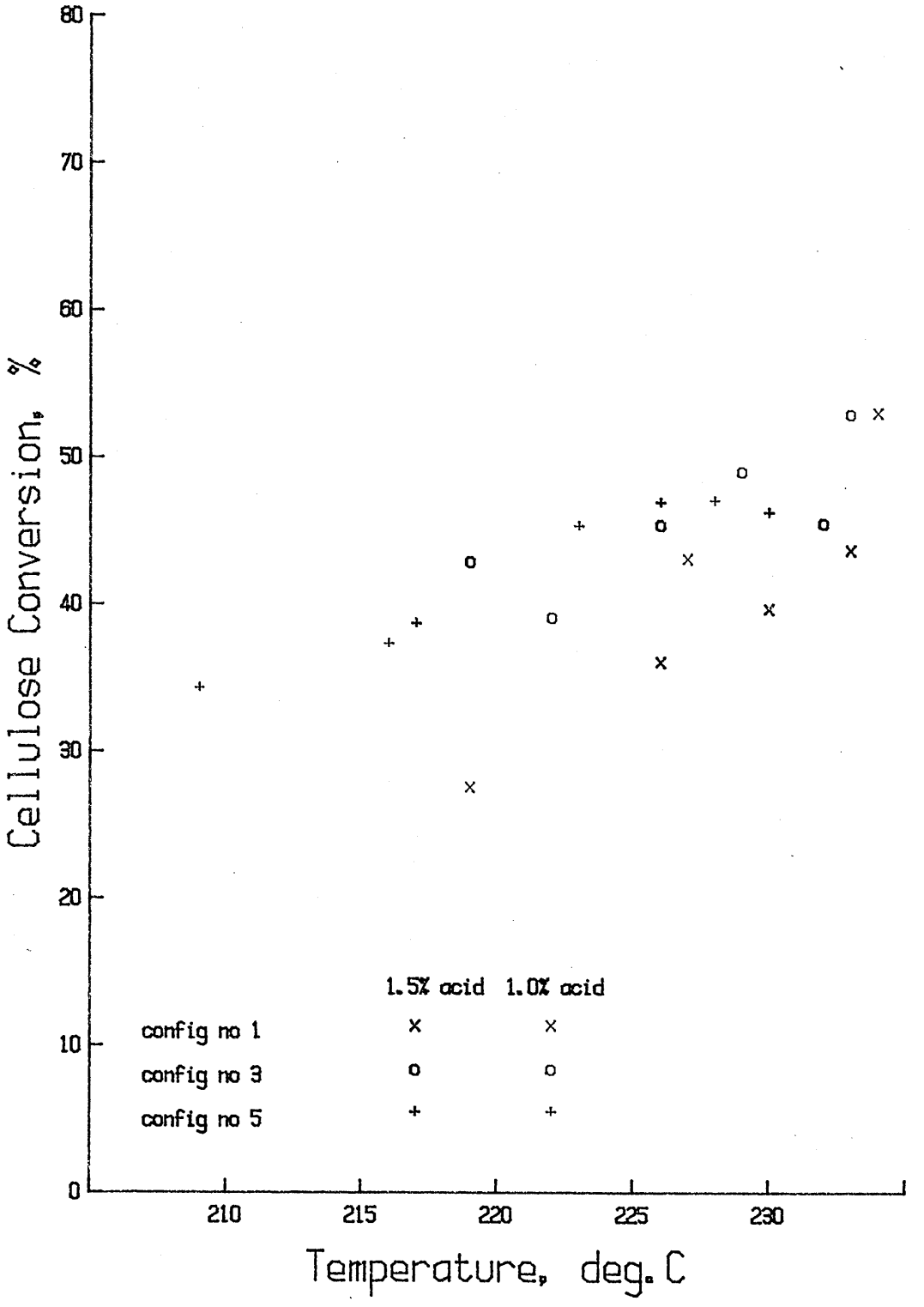

Figure 5.3 (revised). Variation of glucose yield for refuse hydrolysis.

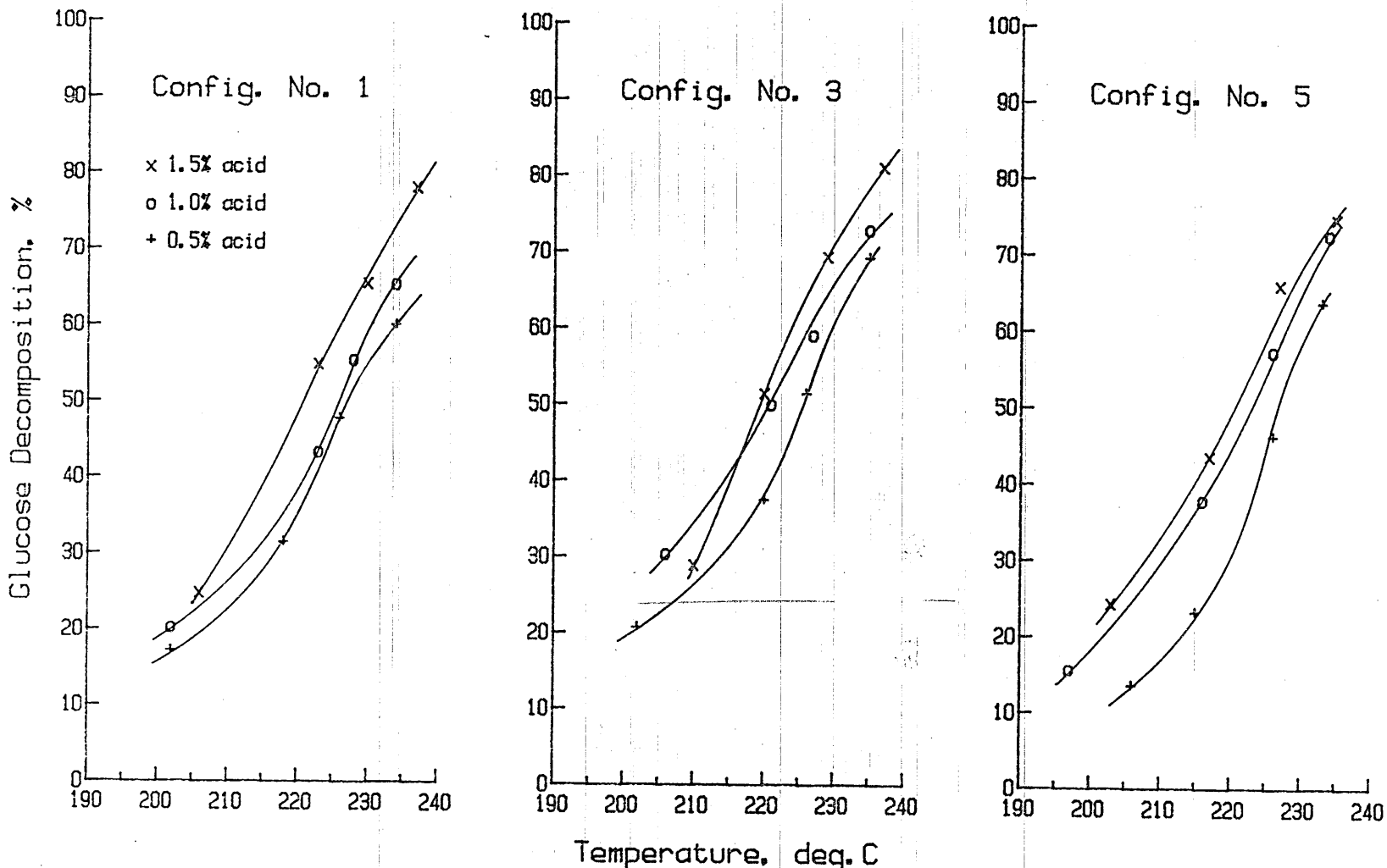

Figure 5.4 (revised). Variation of glucose decomposition with temperature, acid concentration and residence time.